BIOGEOCHEMISTRY OF WETLANDS IN WATERSHEDS AFFECTED BY AERIAL DEPOSITION OF METALS, AND LINKAGES TO AQUATIC ECOSYSTEM RECOVERY.

by

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Abstract

Wetlands are prevalent in the boreal shield, and are efficient at retaining metals and thus modifying the chemistry of downstream receiving waters. The Sudbury region of Ontario, Canada has suffered over a century of elevated metal and sulphur deposition from mining and smelting activity, and wetlands in the area have provided an important ecosystem service by adsorbing large concentrations of metals over decades of emissions. However, metals can be released from peat in some circumstances such as during dry periods that result in a drop in water table height. With emissions declines in the region, there is the potential that wetlands have remained contaminated and are now acting as a source of metals at annual scales. Stream metal concentrations and dissolved organic matter (DOM) exports were evaluated in six Sudbury wetland-draining streams to address the question: Are wetlands in mining-impacted watersheds releasing potentially toxic metals to receiving waters? Water table declines occured in response to summer droughts, and some metals (Al, Co, Cu, Fe, Mn, Ni, and Zn) were released during rewetting events. Other metals that have a high affinity for DOM (Cu, Al, Fe) were also released from some wetlands in the summer in response to mineralization and DOM release. Concentrations in streams exceeded provincial guidelines and fluxes of some metals (e.g. Ni, Co) exceeded atmospheric deposition inputs to lakes by as much as 12 times. Changes in DOM concentration and composition occurred concurrently with the mobilization of metals after drought, with large decreases in aromaticity (SAC_{340}) coupled with decreased DOC concentration. Biotic ligand modelling indicated that these drought-related DOM changes had a large effect on Cu toxicity, and while predicted Ni toxicity increased because of drought-related increases in Ni concentrations, predicted Cu toxicity increased primarily because of drought-related DOM changes. It is likely that these metal stores will take a very long time to deplete,

and this offers important insight into the recovery trajectory of aquatic communities in watersheds affected by smelting. The results can be used to advance restoration efforts in the Sudbury region and other similar smelter-impacted areas affected by aerial depositon of metals.

Keywords

Boreal wetlands, drought, trace metals, smelting, DOM, biotic ligand modelling, toxicity.

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Chapter 1. General Introduction

The production of organic matter in boreal wetlands

Canada's boreal ecozone contains the largest area of undisturbed forest and peatland and represents the largest store of carbon in the world, estimated at over 181 trillion kg (Wells et al., 2011). Twenty-five percent of the world's wetlands are within this ecozone, and many of these wetlands are hydrologically connected to freshwater lakes and rivers (Wells et al., 2011). These lakes, rivers, and wetlands equate to over 80 million ha of freshwater in Canada's boreal forest (Wells et al., 2011), representing almost 90 % of the Canada's freshwater resources, and over 60 % of the world's (Schindler and Lee, 2010). The boreal ecozone is extremely important in regulating future warming by controlling the levels of carbon in our atmosphere, and with this large store of freshwater it is an epicenter of the interaction between climate change and water quality. The economic value of this ecozone in terms of climate regulation, freshwater resources, and ecosystem services has been estimated at around $700 billion US dollars (Wells et al., 2011; Anielski and Wilson, 2009).

There are a wide range of wetland types in the boreal ecozone, but fens and bog peatlands are most common (Wells et al., 2011). Fen peatlands are distinguished from bogs in that they receive inflows from surrounding uplands rather than primarily from precipitation inputs, and so their water chemistry (and therefore plant community composition) is variable depending on local geology. Fens tend to have higher pH and mineral cation concentrations (e.g.: Ca, Mg) than bogs, and have plant communities that are dominated by sedges and grasses. Poor fens have pH and nutrient content intermediate between fens and bogs, with a higher abundance of mosses and shrubs. Both fen and bog peatlands are characterized by organic-rich peat (histols) that are

formed because of higher rates of primary productivity relative to decomposition (Reddy and DeLaune, 2008).

Peat is formed by the decomposition of *Sphagnum* and other plant matter, which first undergoes physical fragmentation and leaching and is then hydrolyzed by microbially-excreted enzymes, releasing monomers including glucose, fatty acids, and amino acids. These monomers undergo either aerobic or anaerobic catabolism by microorganisms, with the characteristic flooding of wetland soils creating low oxygen levels and redox potentials and a dominance of anaerobic catabolism (Reddy and DeLaune, 2008). Organic matter can be oxidized with the use of a wide variety of electron acceptors when oxygen is depleted and anaerobic catabolism dominates (Mitsch and Gosselink, 2000). For example, fermentation involves the use of organic compounds both as electron acceptors and donors, and converts monomers to simple compounds such as lactic acid, and ethanol and carbon dioxide. No additional electron acceptors are required; however the decomposition is not complete and results in the build-up of simple compounds.

The compounds formed during fermentation must be further decomposed by facultative and obligate anaerobes (Reddy and DeLaune, 2008). In anoxic conditions NO_3, MnO_2, and $Fe(OH)_3$ are the preferred electron acceptors for facultative anaerobes, and their reduction results in the oxidation of organic compounds. Upon depletion of these electron acceptors, SO_4 acts as an electron acceptor for obligate anaerobes and sulphate reducers transform sulphate (SO_4) to sulphides, and depending on the reducers, either convert organic compounds to CO_2 and H_2O or to acetate (Mitsch and Gosselink, 2000; Reddy and DeLaune, 2008). In severely anoxic conditions with low redox potentials, methanogens use CO_2, methyl substrates, or acetate as electron acceptors and release methane (CH_4). All of these anaerobic processes are less efficient

than aerobic processes, and so decomposition is slow and partially decomposed material builds up in soils, forming peat.

It has been suggested that anaerobic decomposition in wetlands is slow relative to primary productivity because of oxygen limitations on anaerobic metabolism (Clymo 1992), but also because of the resistance of *Sphagnum* to decomposition (Hogg 1993), as well as low nutrient, and temperature conditions that further limit microbial activity (Frolking et al. 2001; Puranen et al. 1999; Amador and Jones 1993). However, Freeman et al. (2004) propose that decomposition is inefficient simply because of the oxygen limitation of a single enzyme; phenol oxidase. They proposed that the only ubiquitous feature of slow-decomposing wetland systems is the presence of high concentrations of phenolic compounds as a result of the lack of phenol oxidase activity. It is argued that these phenolic compounds interfere with hydrolase activity, further suppressing the decomposition of organic matter (Freeman et al., 2004). Regardless of the mechanism of oxygen limitation on decomposition, pH and temperature depressions both act to further suppress decomposition (Reddy and DeLaune, 2008), and the pool of organic matter that builds up in wetland soils can then represent an important source of organic matter to downstream aquatic systems as well as an important feature of the landscape involved in carbon sequestration and release.

The importance of organic matter to boreal lakes

While the support of lake productivity by wetland-derived organic matter has long been accepted (Wetzel, 1992; Brinson et al., 1981; Goldman 1961), it is now recognized that the importance to overall productivity is much greater than originally suggested by traditional phytoplankton-driven lake model (Prairie, 2008; Vanni et al., 2005; Schindler et al., 1996). The flow of organic

material derived from terrestrial sources can support benthic macroinvertebrates upon which fishes rely (France, 1995), and can even directly support some fish populations (Tanentzap et al. 2014; Mehner et al., 2005; Vanni et al., 2005; Nakano et al., 1999; Goulding, 1980). The landscapes surrounding lakes (watersheds and catchments) supply both particulate organic matter (POM; > 0.45 mm) and dissolved organic matter (DOM; < 0.45 um) to lakes, and wetlands are important sources of these organic materials (Aitkenhead and McDowell, 2000; Dillon and Molot, 1997; Eckhardt and Moore, 1990).

In lakes affected by the aerial deposition of metals, terrestrial POM appears to be particularly important, with direct (as food and/or habitat) and/or indirect effects (via metal complexation and detoxification) on sensitive macroinvertebrates in littoral zones (Rasmussen et al., 2008). Wesolek et al. (2010) found that terrestrial organic matter availability best predicted the community composition of nearshore benthic invertebrate samples in three Sudbury area lakes that have recovered chemically from smelter-related deposition. Wetlands appear to be particularly important sources of terrestrial POM to aquatic communities. In a detailed investigation of a Sudbury watershed, Szkokan-Emilson et al. (2011) found that recovering catchments with more wetland cover discharged a higher ratio of fine POM (FPOM; < 250 µm) to inorganic matter, which was correlated positively with diversity of benthic macroinvertebrates in nearshore areas (Figure 1.1). This FPOM likely acted as a subsidy to the consumer communities, but may also have contributed to the mitigation of remnant metal toxicity by providing a metal-binding substrate and reducing the availability of free metal ions (Szkokan-Emilson et al., 2011).

Dissovled organic matter (DOM) is particularly important to aquatic ecosystems because not only can it support aquatic food webs, but it can regulate light availability and temperature

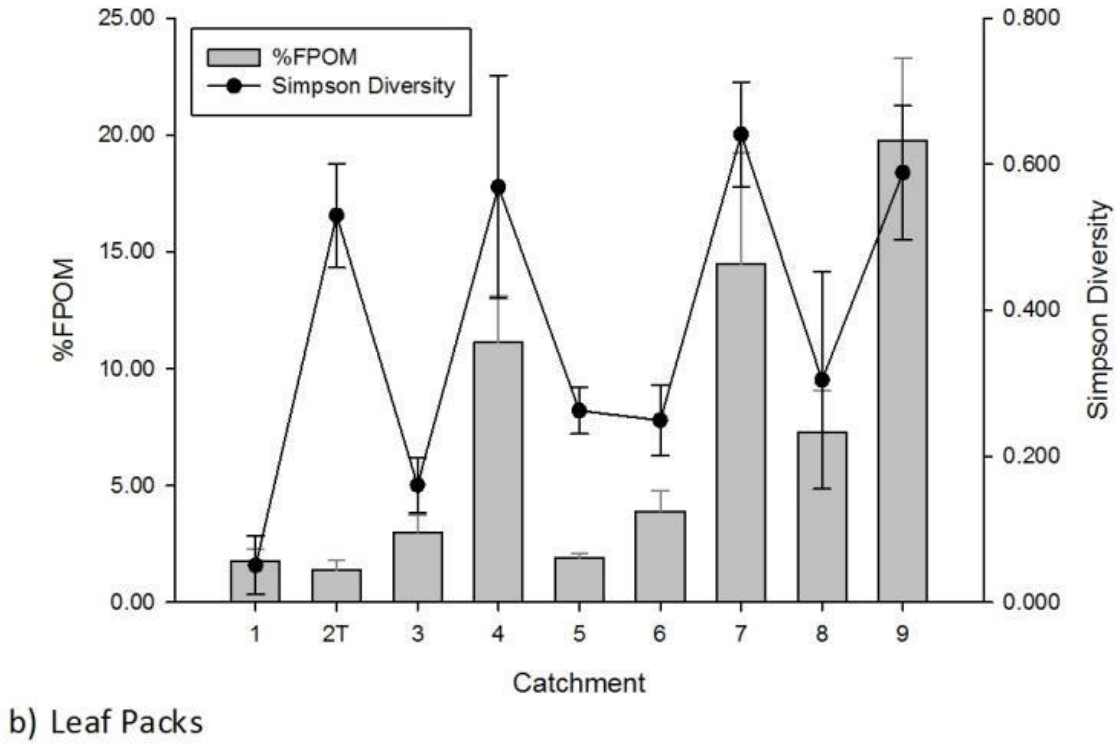

Figure 1.1: Simpson diversity of benthic invertebrates found on deltas closely track the amount of FPOM collected across nine catchment sites in a lake recovering from mining-related disturbances. % FPOM and Simpson diversity are correlated, with % FPOM explaining 50 % of the variation in Simpson diversity in stepwise regressions (from Szkokan-Emilson et al., 2011).

(Snucins and Gunn, 2000; Fee et al., 1996), absorb damaging UV-B radiation (Molot et al., 2004), and regulate the availability of free ion metal ions (e.g.: Doig and Liber, 2006; Watras et al., 1998). DOM is commonly measured as dissolved organic carbon (DOC), but it is a heterogeneous mixture of organic molecules with differing aromaticity, molecular weight, and functional groups. For example, plant-derived DOM is aromatic and has a higher molecular weight and more carboxylic and phenolic functional groups than DOM from autochthonous sources (McKnight et al., 2001).

Wetlands in the Sudbury area are affected by smelter-related metal contamination and appear to be limited in some nutrients (e.g.: P and K; Barrett, 2014). The biogeochemical processes

occurring in these wetlands likely play an important role in regulating fluxes of both metals and DOM as well as the bioavailability and toxicity of metals, but these processes have remained poorly studied in these smelter-affected areas. Seasonal and weather-related changes in DOC concentrations and exports to lakes have also garnered considerable attention (e.g.: Eimers et al., 2008; Laudon et al., 2004; Olivie-Lauquet et al., 2001), however the potential for associated changes in DOM composition and implications to metal toxicity has been less-well studied.

Metals in boreal wetlands

Wetlands are efficient at retaining metals (Brown et al., 2000; Crist et al., 1996). As a result, they are often used as records of past deposition (Martínez-Cortizas et al., 1999; Shotyk et al., 1998; Cole et al., 1990) or are engineered in the form of industrially constructed wetlands to improve downstream water quality (Sobolewski, 1999). Some trace metals originate from natural processes (e.g.: weathering of bedrock), and in many cases can also play an integral part of organic matter decomposition in wetlands. For example, Fe and Mn are reduced during the anaerobic oxidation of organic matter (Reddy and DeLaune, 2008; Lovely et al., 1991), but their reduced forms are highly bioavailable to organisms and can be toxic at high concentrations (Mitsch and Gosselink, 2000). However, metals can be introduced to wetlands from anthropogenic sources via atmospheric deposition of particulate and gaseous phases but also aqueous phases via discharge effluents, and result in peat concentrations that are abnormally high. Wetlands can efficiently hold on to these metals for decades or centuries while they are slowly buried under new-formed peat layers. However, in some cases these peat-bound metals can be released into pore waters and surface waters at concentrations that negatively affect aquatic organisms (Richards et al., 2001), as well as litter decomposition (Johnson and Hale, 2004) and plant secondary chemistry (Jahangir et al., 2008). This is particularly true when soils

are acidic and metals are more likely to become bioavailable (Blake and Goulding, 2002), a common condition of peatland soils. However, as previously discussed, wetlands are also important sources of peat and DOM, and these organic compounds have the potential to affect free ion metal mobility and toxicity. There is a clear need for a study that integrates these processes to mitigate current and future mining-related impacts to boreal wetlands and lakes, as is the direction of this thesis.

Many metals are essential nutrients and are only toxic when at high concentrations in a state that is bioavailable. For example, Cu is an essential nutrient (Mertz, 1981) that exists in three redox-controlled oxidation states with Cu^{2+} being the most common and a highly mobile form (Mitsch and Gosselink, 2000). This free ion form can impair protein function and gill exchange in aquatic organisms at high concentrations (Grosell et al., 2002). The speciation of metals is complex, and the availability of free ion metals is controlled not only by redox state but also through interactions with other anions such as carbonate, chloride, and functional groups on organic ligands (both peat and DOM) that bind free metals (Paquin et al., 2002; Brown et al., 2000; Crist et al., 1996). Organic molecules can have several negatively charged functional groups, and the binding and/or chelation of metals with these organic molecules can result in their removal from pore waters (to peat), or the formation of dissolved complexes that are less available for biological uptake or that precipitate out of solution (Richards et al., 2001). For metals such as Cu that have a high affinity for organic molecules, over 98 % can be present as organic complexes (Sauvé et al., 2000). The uptake of available free-ion metals by organisms (and therefore toxicity) is also regulated through interactions with other cations (e.g.: Ca, Mg) and protons that compete for exchange sites on the biotic ligand (Paquin et al., 2002). Several speciation models have been developed to predict the availability of free-ion metals in the absence of direct

measures (e.g: WHAM; Tipping, 1994), and the biotic ligand model (BLM) has incorporated interactions with biotic ligands to predict toxicity to aquatic organisms (Paquin et al., 2002; Richards et al., 2001) and plants (Antunes et al., 2007).

Short-term events

Severely disturbed watersheds with little remaining vegetation can have low water retention potential, and short-lived or episodic runoff events may be common (Buttle et al., 2000). Typically in many monitoring programs stream water sampling occurs at intervals of every 2 to 4 weeks, with the potential to miss short-lived events that are likely to be quite common. Storms and other episodic events can for instance result in short spikes of high concentrations, and missing these events can seriously affect the accuracy of flux estimates (Rucker and Schautzer, 2010). This problem is likely exacerbated in systems with wetlands that suffer large water table fluctuations (worsened by regional drought conditions), because nutrient, metal, and base cation concentrations in streams draining organic soils are strongly influenced by short-term rewetting events following drought (Adkinson et al., 2008; Tipping et al., 2003). It has been suggested that a sampling frequency of less than 3 days may be necessary to capture changes in water chemistry parameters that can be highly temporally variable (Adkinson et al., 2008; Semkin et al., 1994).

Even in locations remote from industrial sources, metal concentrations in wetland-draining streams can exceed water quality guidelines following drought-related water table declines in the summer, and these metals can be highly bioavailable due to acid-induced metal leaching via sulphur oxidation (Landre et al., 2009; Adkinson et al., 2008). In the Sudbury area, acid-pulses have been shown to occur in lakes following water level declines that result in the exposure of littoral zone sediments, and these events can have important implications for biological recovery

(Arnott et al., 2001; Yan et al., 1996). More detailed sampling of wetland stream runoff is therefore required to identify whether episodic changes in chemistry from peat metal pools can have dramatic contributions to the delayed biological recovery in lakes of disturbed watersheds.

Study Outline and Objectives

The Sudbury region of Ontario, Canada has suffered decades of metal and sulphur deposition from the mining and smelting activity in the area. Sudbury smelters were once the highest point source of S in the world, with annual sulphur dioxide (SO_2) emissions peaking at 2560 kilotonnes in 1960. Metal particulate deposition was also very high, exceeding 10s of thousands of tonnes annually and resulting in extensive contamination of soils and surface waters in the area (Keller et al., 2007; Potvin and Negusanti, 1995). Soil metal levels exceeded provincial guidelines in the area (Meadows and Watmough, 2012), and wetlands were also affected with metal levels high enough to be toxic to plant life (Taylor and Crowder, 1983). Major reductions (>95 %) in atmospheric emissions of pollutants have occurred because of improved technologies and more stringent regulations in recent decades and widespread improvements in surface water chemistry have been observed. Despite these improvements, metal contamination persists in many areas and biological recovery of lakes and streams has been significantly delayed (Keller et al., 2007; Nriagu et al., 1998). This heavily disturbed industrial area is also susceptible to drought because of thin soils,, and reduced vegetation cover, and so it is likely that flashy events and water table fluctuations in peatlands will be more persistent and of higher magnitude in these areas as a result.

Wetlands are abundant in boreal ecozone where mining operations are ongoing, and there are over 33,000 ha of wetlands in the city of Greater Sudbury alone (Monet, 2013). In landscapes

recovering from widespread vegetation and soil loss, such as the smelting-impacted landscapes of Sudbury, wetlands sometimes represent isolated pockets of organic soils and vegetation among otherwise barren or lichen-covered rocks. Peatlands are common in the area, and they differ in baseline chemistry and range from minerotrophic rich fens and mesotrophic poor fens to ombrotrophic bogs (see Pennington, 2014). Many of these wetlands operate at the interface between terrestrial and aquatic ecosystems, and fens often have outflows draining directly into surface waters such as lakes and rivers. Several of the wetlands in Greater Sudbury are directly connected to the 47,000 ha of lakes, rivers, and streams in the area (Monet, 2013), and there is obvious potential for wetlands in this mining impacted landscape to mediate terrestrial linkages to aquatic ecosystem recovery.

Despite the likelihood that wetlands play an integral role in the recovery of aquatic ecosystems, few studies have investigated the function of boreal wetlands in terms of regulating organic matter and metal fluxes in watersheds that are recovering from disturbance. Even fewer studies have attempted the high-frequency sampling required to capture short term events that may be highly influential in such systems (Kerr et al., 2008). Sudbury offers a unique environment to test several theoretical and applied hypotheses because of large spatial and temporal variation in water chemistry and watershed conditions. This thesis makes use wetlands in smelter impacted catchments to attempt to better understand the cycling, export, and potential toxicity of metals in relation to DOM from disturbed wetlands. A preliminary survey of vegetation and annual water table fluctuation in 29 wetlands was conducted in the region in 2010, and peat samples were collected from a subset of 18 wetlands revealing a wide range in metal and nutrient content (primarily poor and transitional fens) (Appendix A1; see also Pennington, 2014). Six of these wetlands were selected because they represented the range of surface peat conditions observed in

the regional survey, with sites at the low-ends and high-ends of metal and nutrient concentrations observed regionally (Appendix A1). They were also selected because they had an outflow stream draining directly into a lake with a recovering aquatic community and were within 15 km of the active Copper Cliff smelter, however these wetlands would have also been affected by other smelters in the area including the Coniston smelter that ceased operation in 1972. Four of the sites were fens with deep organic layers (> 50 cm) and were dominated by shrubs (primarily *Chamaedaphne calyculata*), sedges, and rushes, but these sites (and other Sudbury wetlands) have relatively low *Sphagnum* cover (Barrett, 2014). The other two wetlands (D4 and D5) had shallow organic layers (~ 30 cm) overlying mineral soils, with a variety of grasses more characteristic of wet meadows (primarily *Muhlenbergia uniflora* at D4 and *Calamagrostis canadensis* at D5) and some terrestrial grasses at D5 as well (mostly *Schizachne purpurascens*) (See sites in Figure 1.2 and Figure 1.3).

Given the benefits that wetlands provide to lakes in terms of metal retention and water quality regulation, and the potential for release of these retained metals, this thesis addresses the research question: Are wetlands in mining-impacted watersheds releasing toxic metals to receiving waters that could be lending to delayed recovery of aquatic communities? The objectives of the thesis are to quantify metal release from wetlands in watersheds affected by aerial deposition of metals, identify key mechanisms of metal release, and determine the importance of DOM and metals released from wetlands to the potential toxicity of recieving waters.

It was hypothesized that with the efficient retention of metals by wetlands over several decades and with recent improvements in smelter emissions since the 1970's, Sudbury area wetlands have now become sources of metals to receiving waters. In Chapter 2, trace metal and

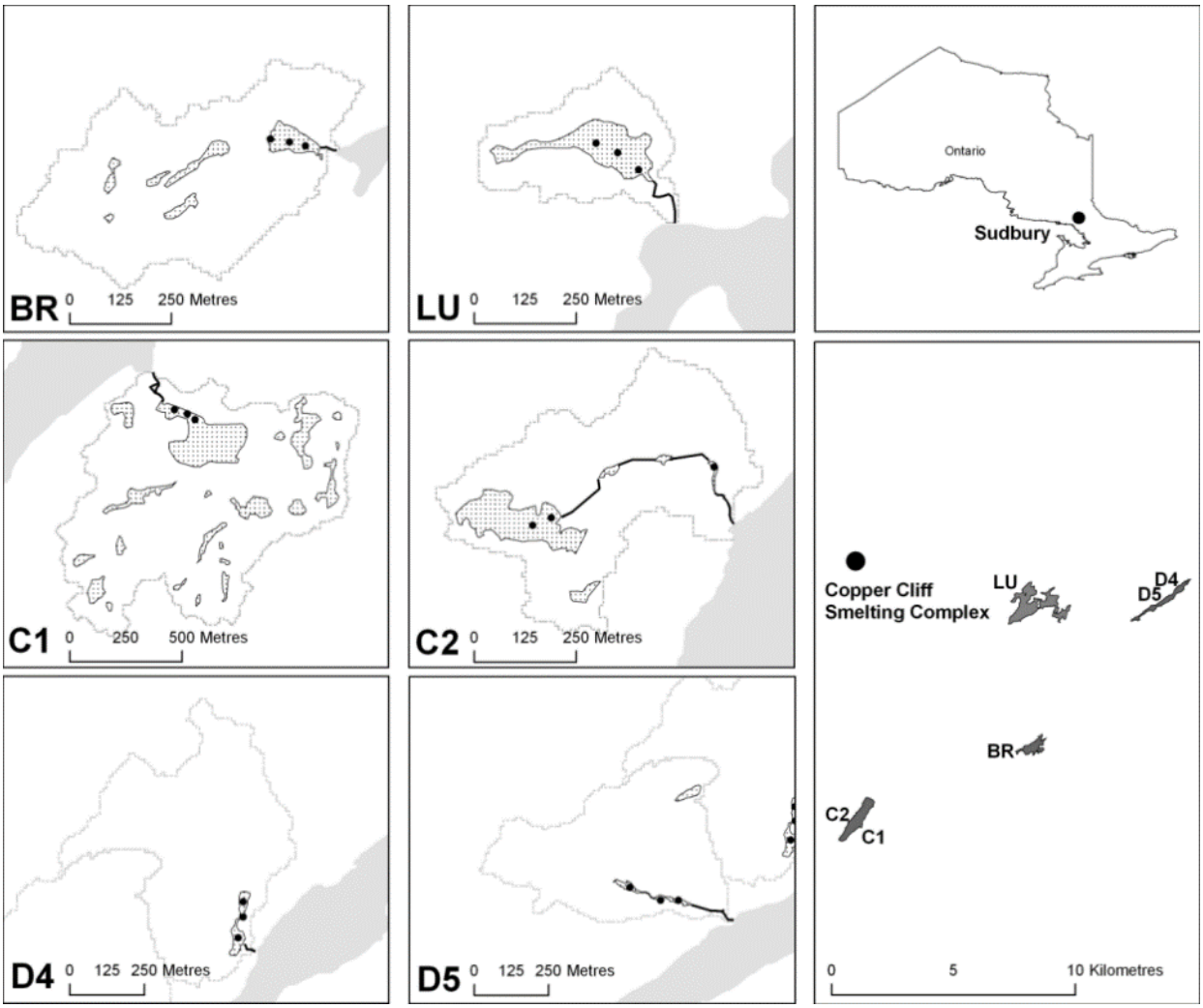

Figure 1.2: Locations of six wetlands selected for this thesis relative to the Copper Cliff Smelter. The catchments are delineated and the catchment-draining streams are shown. Black points mark sampling stations within the wetlands. The abandoned Coniston smelter is not shown but lies approximately 4 km to the Northeast of D4 and D5.

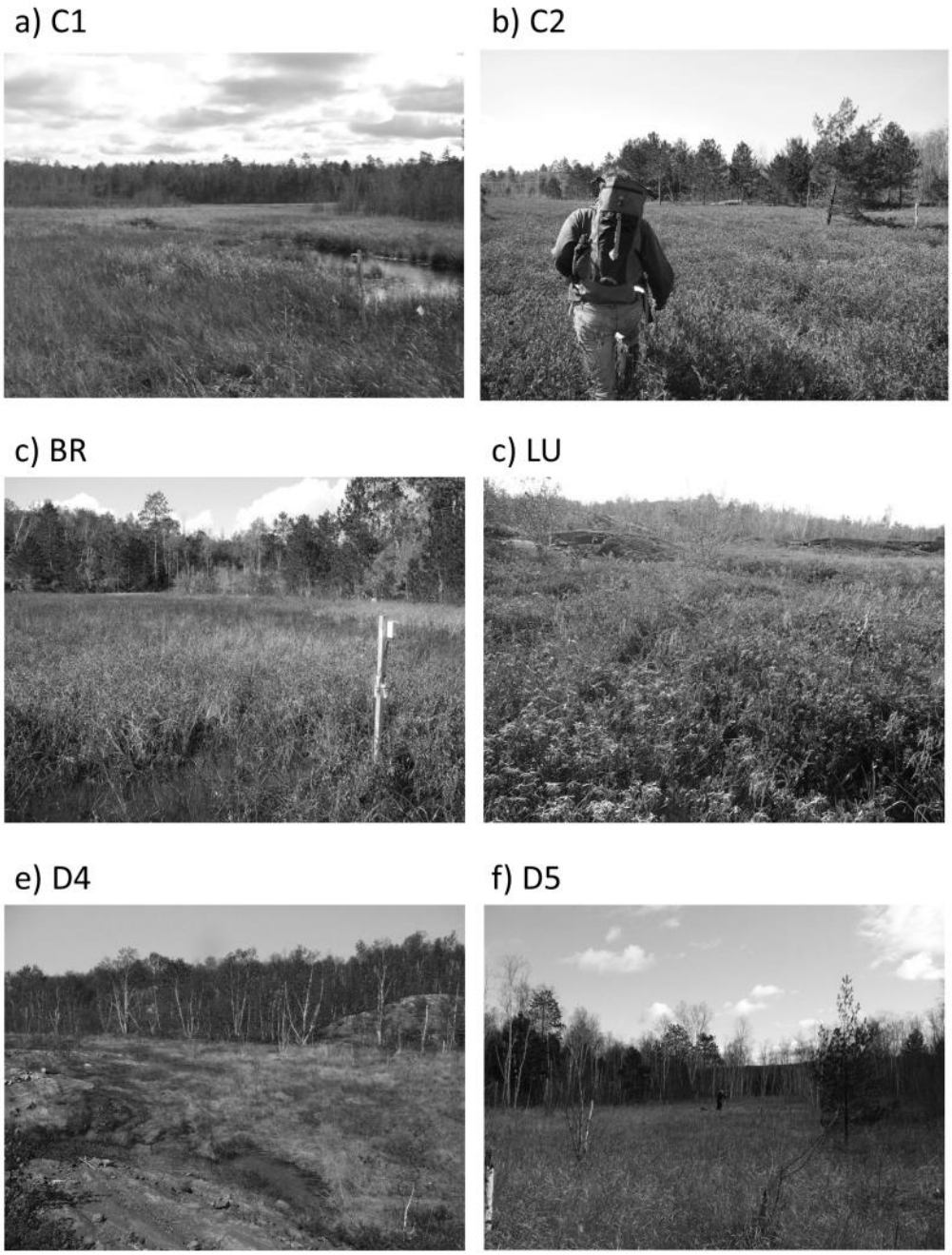

Figure 1.3: Photos of the six wetlands selected for this thesis. Sites C1 (a), C2 (b), BR (c), and LU (d) are dominated by shrubs and sedges, and sites D4 (e) and D5 (f) are dominated by grasses and sedges.

base cation catchment-budgets are calculated for six wetland-influenced catchments in the Sudbury area. It was predicted that current aerial deposition of metals is reduced and that exports from internal losses would exceed these inputs, and that these budgets would reveal a net loss of metals at annual scales. It was expected that these losses would largely be a result of water table fluctuations and oxidation processes, and so controls on metal release from wetlands were also investigated during this two-year period by sampling aerial deposition inputs, wetland pore water, and stream outflow chemistry concurrently. In chapter 2, ordination techniques are used to identify biogeochemical indicators of metal release through time, and volume-weighted concentrations of metals in outflow streams are related to these biogeochemical indicators with regression analyses. Results are also discussed in terms of wetland-related metal loads to lakes relative to current depositional inputs from smelters.

It was hypothesized that large amounts of metals would be released at high concentrations in episodic events following water table declines during warm, dry summer months. Chapter 3 uses high frequency sampling to evaluate the chemical changes during the summer and fall of 2011 in streams draining from two of the six wetland-influenced catchments. Stream outflow samples are collected with ISCO automated samplers (every 8 hours) from June 2011 to November 2011 to detect and quantify peak concentrations of metals during short-term rewetting events in response to a summer drought that occurred that year and resulted in large water table declines in the wetlands. Associations between metals and other chemical parameters in stream water were explored with ordination techniques to investigate the drivers of drought-related metal release. As sulphur oxidation is considered the primary mechanism of metal release in response to water table declines, SO_4-related fluxes during these short-term events were quantified and contrasted with the flux of DOC-related metals during the drought. It was expected that if drought-related

release was occurring, that SO_4-mediated re-acidification events would result in the release of high concentrations of metals over relatively short time periods (i.e.: days to weeks) but would also be responsible for large fluxes of metals compared to DOC-related release.

It was hypothesized that the metal releases discussed in Chapter 3 would be coupled with changes in dissolved organic matter (DOM) composition and concentration that would result in highly toxic conditions in outflow streams and receiving waters. Chapter 4 investigates drought-related changes in DOM concentration and composition in the six wetland-draining streams to evaluate the role of DOM on potential metal toxicity. Parallel factor analyses (PARAFAC) of fluorescence Excitation-Emission Matrices (EEMs) and spectral absorbance measures are used to evaluate DOM composition, and potential toxicity is modelled with the biotic ligand model (BLM). The influence of DOM on modelled toxicity is determined by adjusting the BLM to exclude changes in composition and concentration, and the influence of this toxic outflow into receiving waters is estimated by mixing lake and stream water and modelling changes in toxicity. It was predicted that decreased DOM concentration would be responsible for an increase in predicted toxicity because of increased free ion metal, and that this will be exacerbated by a loss in DOM metal binding capacity (as estimated with aromaticity).

This study is also designed to aid in management activities. Chapter 5 summarizes the goals and conclusions of the thesis and suggests remediation and management options based on the findings. A schematic for prioritization of locally significant wetlands is also established to aid in management decisions.

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Chapter 2. Wetlands as long-term sources of metals to receiving waters in smelter-impacted watersheds in Sudbury, Canada[1]

Abstract

Wetlands are prevalent in the Sudbury, Ontario region and often operate at the interface between terrestrial and aquatic ecosystems, modifying water chemistry and potentially affecting the recovery of impacted lakes. The deposition of metals and sulphur in Sudbury in 2010 to 2012 was far below that reported in the 1970's, but still higher than regional background values. Wetlands in the area have accumulated large quantities of metals, and high concentrations of these metals were discharged in streams primarily in response to SO_4-related acidification events or associated with high dissolved organic carbon (DOC) production in early summer. Concentrations of most metals in streams exceeded provincial guidelines and fluxes of some metals from catchments exceeded deposition inputs to lakes by as much as 12 times. The release of metals long after emissions reductions have been achieved must be considered in ecosystem recovery studies, particularly as dry conditions may become more prevalent in boreal regions affected by smelting.

[1] Szkokan-Emilson, E.J., Watmough, S., Gunn, J.M., 2014. Environmental Pollution 192, 91-103.

Introduction

Wetlands retain atmospherically deposited metals through ionic exchange with organic matter (Brown et al., 2000; Crist et al., 1996) and are often used as records of past deposition (Martínez-Cortizas et al., 1999; Shotyk et al., 1998; Cole et al., 1990) or are constructed to improve downstream water quality (Sobolewski, 1999). It is estimated that 25 % of the world's wetlands are in Canada's boreal region, and a wide range of wetland types exist in this area, although fens and bogs are most common (Wells et al., 2011). Some of these boreal wetlands have been and/or will be subject to elevated metal deposition, particularly those near localized mining and smelting activity (Wells et al., 2011). Elevated metal concentrations in peat have been reported in wetlands near smelters in Ontario (Gignac and Beckett, 1986; Taylor and Crowder, 1983), Quebec (Kettles and Bonham-Carter, 2002), and Manitoba in Canada (Outridge et al., 2011), as well as in parts of Finland (Nieminen et al., 2002) and the Czech Republic (Novak et al., 2011). These wetlands are often at the interface between terrestrial and aquatic systems and can affect surface water quality in downstream systems.

Although wetlands retain metals, they can also become sources of metals to surface waters under certain conditions. For example, reductions in pH can result in a release of metals from peat through competition of binding sites between metal cations and protons (Brown et al., 2000; Gambrell et al., 1991). When dry periods result in a lowering of the water table, sulphur (S) can become oxidized to sulphate (SO_4) and subsequent rewetting events then lead to the formation of sulphuric acid (Eimers et al., 2007, 2003; Devito and Hill, 1999). The associated protons compete for binding sites and can result in the release of metals (Juckers and Watmough, 2013; Tipping et al., 2003; Lucassen et al., 2002), and releases have even been documented hundreds of kilometers from the originating smelters (Landre et al., 2009; Adkinson et al., 2008). Increases

in ionic strength in response to other sources of ions (e.g.: road salts) can also affect metal binding capacity (Löfgren, 2001; Amrhein et al., 1992). Some metals will also preferentially bind to dissolved organic ligands and form mobile organo-metal complexes, so seasonal increases in dissolved organic carbon (DOC) concentration can result in increased mobility of metals (Cory et al., 2006; Antoniadis and Alloway, 2002; Olivie-Lauquet et al., 2001). Furthermore, wetlands can be significant sources of metals derived from within the catchment (e.g.: Fe, Mn, and Al) during periods of high groundwater infiltration (Shotyk, 1988).

The mining region of Sudbury, Canada is one of the most widely-studied boreal regions in the world in terms of acid- and metal-impacts, emissions reductions, and subsequent wide-scale ecosystem recovery. Over a century of smelter emissions resulted in elevated deposition of S and metals in the region, including Cu, Ni, Co, Zn, Fe, Pb, Cr, and Cd (Adamo et al., 2002; Hazlett et al., 1984; Hutchinson and Whitby, 1977). Major reductions (> 95 %) in atmospheric emissions of pollutants have occurred since the 1970s, but soils and surface waters remain contaminated in many areas (Meadows and Watmough, 2012; Keller et al., 2007; Nriagu et al., 1998). Improvements in terrestrial and aquatic ecosystems are well documented in Sudbury (Keller et al., 2007; McCall et al., 1995), and research in the area has contributed to our understanding of natural recovery processes and restoration efforts elsewhere (Kozlov and Haukioja, 1999; Schindler, 1997). There are over 33,000 ha of wetlands in the city of Greater Sudbury, many of which are connected to the 47,000 ha of lakes, rivers, and streams in the area (Monet, 2013). Although it is known that wetlands close to the smelters were contaminated with metals in the 1980's (Gignac and Beckett, 1986; Taylor and Crowder, 1983) and that they play an important role in modifying surface water quality, the biogeochemistry of these wetlands and their impact on water quality has remained relatively understudied.

The objective of this study was to examine the biogeochemical variability of mining-impacted catchments with a range of characteristics to identify key metal-regulating processes that may be occurring regionally. The focus is on catchments with wetland outflows draining into lakes, because of the potential for metals released from these wetlands to affect aquatic communities in receiving waters. Four questions are addressed: (Q1) How does current deposition of smelter-related metals and S compare with historical deposition in Sudbury? (Q2) What are the biogeochemical processes governing the spatial and temporal variability of pore water chemistry? (Q3) Is the stream outflow chemistry from these catchments related to pore water chemistry, and does this result in high concentrations of metals in outflow streams? And finally (Q4), are these wetland-influenced catchments currently losing or retaining metals? The implications of these results are discussed in terms of potential toxicity and metal loads to receiving waters, and the information gained will be applicable to other boreal regions where localized mining-related impacts are ongoing and expanding and climate is also changing.

Methods

Site selection and characterization

A preliminary survey of vegetation and annual water table fluctuation in 29 wetlands was conducted in the region in 2010. Peat samples were collected from a subset of 18 of the wetlands (primarily poor or transitional fens) revealing a range in metal and nutrient content (Appendix A1). Six of these wetlands were selected because they represented the range of surface peat conditions observed in the regional survey, with sites at the low-ends and high-ends of metal and nutrient concentrations observed regionally (see Appendix A1). They were also selected because they were in a watershed sub-catchment with an outflow draining directly into a lake with a

recovering aquatic community (henceforth termed "wetland-influenced catchments"). They were all within 15 km of the active Copper Cliff smelter, however these wetlands would also have been affected by the Coniston smelter that ceased operation in 1972 (Table 2.1). Two of the wetlands (D4 and D5) had shallow organic soil layers (~ 30 cm) overlaying mineral soils and had lower organic matter content. These wetlands were dominated by a variety of grasses more characteristic of wet meadows (primarily *Muhlenbergia uniflora* at D4 and *Calamagrostis canadensis* at D5) with some terrestrial grasses at D5 as well (mostly *Schizachne purpurascens*). The other four wetlands were more characteristic of poor fens, had deep organic layers (> 50 cm), and were dominated by shrubs (primarily *Chamaedaphne calyculata*), sedges, and rushes.

The catchments were delineated with Whitebox Geospatial Analysis Tools (Lindsay, 2012) using digital elevation models compiled in ArcMap (ESRI ArcGIS version 9.3, Redlands, CA) from Ontario Basic Mapping and Ontario Ministry of the Environment Forest Inventory data. Wetland areas and stream lengths were interpreted from 1:40,000 aerial photos (taken by the City of Greater Sudbury) and corrected with in-field data. The catchments vary in distance from the smelters, total area (11.0 to 100 ha), proportional wetland area (1.39 to 20.8 %), and length of the outflow to the lake (45.0 to 156 m) (Table 2.1, Figure 2.1). They are all in an area of heavy historical smelter-related aerial deposition but the extent of damage to upland vegetation varies among sites. Catchments LU, D4, and D5 are in an area that was classified as barren to semi-barren, impacted primarily by fumigation from the active Copper Cliff smelter and the now-closed Coniston smelter (McCall et al., 1995). The Daisy Lake catchments (D4 and D5) suffered a loss of pine-dominated forest in the 1940's followed by severe erosion of upland soils. The uplands at these sites remain sparsely vegetated, and the lowland forests are dominated by early-successional deciduous trees (Szkokan-Emilson et al., 2011; Dixit et al., 1996). LU is in an

Table 2.1 Catchment characteristics and mean (SD) concentrations of metals, cations, and nutrients in the wetlands of six catchments. Five peat samples were taken at surface (0-15 cm depth) and are compared to the medians and ranges from a 1981 survey of 25 wetlands in the Sudbury area (Taylor and Crowder 1983). The pH is given as a mean from pore water samples collected across the two study years. Distances to nearest smelter are given from either [1] the active Copper Cliff Smelter or [2] the abandoned Coniston smelter.

	C1		C2		BR		LU		D4		D5		1981 Median (Range)	
Metals and other cations (mg/kg)														
					1045									
Al	5345	(1738)	1716	(50.8)	6	(2589)	3356	(777)	20950	(4503)	18618	(2683)		
Co	9.35	(3.32)	8.36	(0.200)	10.4	(0.888)	17.3	(4.35)	11.8	(1.52)	12.0	(1.57)		
Cu	844	(179)	635	(83.3)	1039	(143)	1238	(428)	711	(183)	512	(116)	371	(21-6912)
Fe	7656	(2660)	8179	(2177)	3091	(108)	7866	(733)	15290	(812)	17272	(4137)	12452	(2090-45448)
Mn	39.2	(5.88)	29.1	(0.590)	42.5	(7.75)	47.1	(13.8)	62.5	(22.6)	92.4	(12.8)	188	(25 - 573)
Ni	472	(193)	348	(11.2)	540	(47.2)	920	(231)	275	(47.2)	429	(186)	481	(38 - 9372)
Zn	42.9	(15.7)	38.7	(8.08)	43.0	(12.6)	64.7	(20.2)	41.3	(14.0)	45.2	(2.14)	92	(23-481)
Na	507	(106)	705	(84.0)	572	(57.2)	1245	(336)	491	(194)	468	(28.2)		
K	674	(96.1)	834	(240)	591	(61.2)	1019	(171)	1044	(399)	1117	(197)		
Ca	2524	(603)	5432	(1043)	1741	(294)	5837	(2326)	723	(159)	1727	(403)	15575	(2650 - 38068)
Mg	586	(127)	385	(13.5)	384	(42.9)	403	(68.6)	1721	(978)	2315	(533)	2775	(683 - 7220)
Nutrients and pH														
% C	31.8	(4.34)	48.4	(1.24)	39.6	(2.28)	49.2	(0.490)	17.3	(3.40)	12.1	(5.83)		
% N	1.31	(1.04)	1.73	(0.234)	2.11	(0.204)	1.86	(0.230)	1.34	(0.212)	0.713	(0.260)		
% S	0.390	(0.339)	0.695	(0.159)	0.756	(0.093)	0.675	(0.094)	0.238	(0.065)	0.224	(0.103)		
pH	4.85	(0.436)	4.08	(0.566)	4.83	(0.459)	4.20	(0.623)	4.22	(0.460)	4.86	(0.480)	NA	(3.6 - 5.6)
Catchment Characteristics														
Area (ha)	100		27.5		26.8		11.0		32.4		29.2			
% Wetland	13.5		10		5.15		20.8		1.39		1.64			
Stream length (m)	145		92.0		45.0		156		48.0		148			
Nearest smelter (km)	12.8[1]		12.2[1]		11.6[1]		7.30[1]		4.1[2]		4.6[2]			
Receiving Lake	Clearwater		Clearwater		Broder 23		Laurentian		Daisy		Daisy			
Lake Area (ha)	76.0		76.0		36.9		157		36.6		36.6			

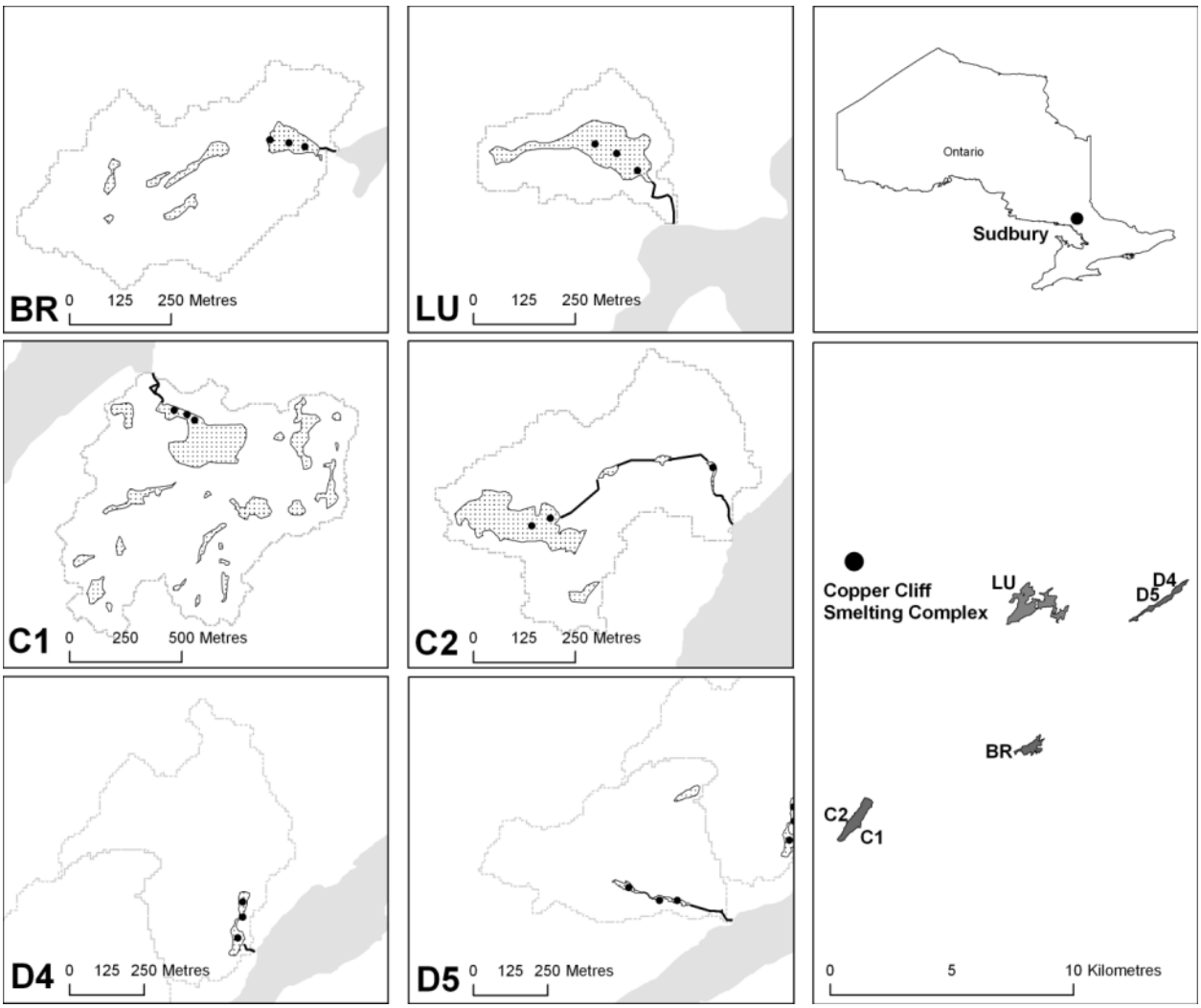

Figure 2.1: Map of six wetland-influenced catchments in the Sudbury area with streams draining into receiving lakes. Wetland sampling stations are indicated with a solid circle. The active Copper Sliff smelter is located at 46°28'49.49"N, 81°3'23.66"W, and the abandoned Coniston smelter (not shown) is at 46°28'47.94"N, 80°50'29.05"W.

intermediate area with some disturbance to upland vegetation and some soil loss. Catchments C1, C2, and BR are in an area with less-severe soil loss or impact to upland vegetation and their forests are comparatively diverse with a variety of coniferous and deciduous trees (McCall et al., 1995). Two catchments (C1 and C2) were gauged for mass-balance studies in the late 1970's, investigating the impacts of smelters on lakes and watersheds in the Sudbury area at that time (e.g.: Jeffries, 1984; Jeffries et al., 1984; Scheider, 1984).

Wetland peat

Three sampling stations were spaced evenly in each wetland from 40 m to a maximum of 160 m from the outflow stream along transects, focusing sampling where influence on outflow would be greatest. The outflow stream at C2 also ran through a small riparian wetland, so an exception was made and one of the stations was established in the riparian wetland as well (Figure 2.1). HOBO™ water sensors and temperature loggers were installed at each station at 10 cm depth and a second set at 30 cm depth in the peat, and set to record at 15 minute intervals, from which daily and monthly averages were calculated. Peat samples were collected in 2012 within the top 15 cm at each of the three stations, with two additional samples taken between the stations at all sites (5 total). The peat was digested with trace grade HNO_3 at 100 ^oC for 8 hours and diluted with MilliQ water to 2 % HNO_3. Analysis was done with a PerkinElmer Optima 7000DV ICP-OES (Al, Ca, Co, Cu, Fe, K, Mg, Mn, Ni, P, Zn) and an ELEMENTAR combustor for % C, N, and S. NIST-1515-SRM apple leaves were included to verify accuracy and precision, and recoveries ranged from 85 to 98 %. Note that only the surface peat (upper 15 cm) is discussed in this chapter for comparison to historical data and for relevance to depositional inputs, however 15-30 cm peat data is available in Appendix A2 and is used for pool size calculations in Chapters 3 and 5.

Stream flow and water table height

Stream water levels were recorded at 15 minute intervals with HOBO™ U20 loggers in the outflow streams, and water table height was recorded at 15 minute intervals using TruTrack™ WT-HR 1000 Water Level Loggers installed in a well in each wetland from 0.70 m below ground to 0.30 m above ground. Stream flow was measured across a range of water heights over two years using a Marsh-McBirney Flo-Mate™ 2000 velocity meter. Power rating curves were generated for each catchment, yielding R^2 values of 0.95, 0.95, 0.92, 0.94, 0.98, and 0.99 for C1, C2, D4, D5, BR, and LU respectively. Discharge for each 15 minute period was estimated from the rating curves and summed to daily totals. Flows were modelled for the ice-covered months (December to March) using the BROOK90 v4.5 hydrologic model (Federer, 2002), incorporating daily meteorological data (Environment Canada, 2013) and measured discharge data. The model was constructed for the entire two-year study period, and Nash-Sutcliffe coefficients of efficiency of 0.59 and 0.69 were obtained for daily and monthly data respectively, above the suitable cut-off of 0.5 suggested by Moriasi et al. (2007). Modelled winter discharge and measured discharge was then summed to total monthly and annual volumes for calculation of fluxes and volume-weighted concentrations (VWCs). All rating curve and BROOK90 modelling data are shown in Appendix A3.

Bulk deposition, pore water, and outflow samples

Bulk deposition was collected at each catchment in samplers constructed of 30.5 cm diameter polyethylene funnels draining into polyethylene bags through 80 μm Nitex filters, and placed 1 m above the ground in the middle of the wetland. Winter deposition was collected in a polyethylene bag in a 35 cm deep open bucket (30.5 cm diameter), and thawed and filtered

through an 80 μm Nitex filter. Deposition volume was measured and a 300 ml subsample was kept for analyses. The loss of a sample was rare, but values from the nearest neighboring collector were used when it occurred.

Pore water was collected from two sampling wells at each of the three stations in the wetlands (see *Wetland Peat*). The preliminary survey of 29 wetlands found mean water table fluctuation to be 24.2 cm (SD of 12.6 cm) with average minimum water table heights of 23.0 cm below soil surface (Appendix A1), so samples were restricted to the upper 30 cm in each wetland. A 100 ml sample was extracted from a well in the upper 10 cm of peat, and 200 ml from a well in the 10 to 30 cm layer, and the two were pooled into a single 300 ml sample from each of the three stations to address the concern that a single 0 to 30 cm well would be biased by the porous upper layer. Small 1.9 cm diameter PVC pipes (3mm slit openings covered in nylon mesh) were used to minimize atmospheric oxygen exposure, and samples were extracted from wells with polyethylene syringes and tubing after purging the well three times.

Two 300 ml stream water samples were collected: one immediately below the wetland ("wetland outflow" sample) and a second one immediately above the outflow to the lake ("catchment outflow" sample). All samples (pore water, wetland outflow, catchment outflow, and bulk deposition) were collected concurrently every 2 to 4 weeks (depending on rain events and availability of water) from October to September of 2010 to 2011 and 2011 to 2012. pH was measured *in-situ* with a Hannah Instruments HI 991003 portable meter and HI 1297 probe, and samples were filtered with 80 μm Nitex mesh and stored in Nalgene bottles until filtration with 0.2 μm VWR Nylon syringe filters. A portion of the sample was acidified with trace-grade HNO_3 and analyzed for total dissolved metals (Al, Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Zn) and base cations (Ca, K, Na, Mg) using a PerkinElmer Optima 7000DV ICP-OES. Un-acidified portions

of the samples were analyzed for NH_4-N with a Bran+Luebbe AutoAnalyzer3 spectrophotometer, SO_4-S and NO_3-N with a DIONEX ICS 1100 ion chromatographer, and DOC and DIC with a Shimadzu TOC-VcpH analyzer. All containers and equipment were washed in a 10 % HCl acid bath and rinsed with MilliQ water between collections. Cadmium, Cr, and Pb were below detection limits (0.100, 0.100, and 1.00 µg/L respectively) in all but a few samples and were excluded from further analyses. Smelter-related metals are defined as those that have been emitted from local smelters (Co, Cu, Fe, Ni, Zn) (Adamo et al., 2002; Hutchinson and Whitby, 1977), and catchment-derived metals as those only mobilized from within catchments via soil erosion and leaching (Al, Mn).

A Procrustean randomization test (PROTEST) with 10,000 permutations was performed to assess association between wetland outflow chemistry, catchment outflow chemistry, and pore water chemistry, standardizing to give equal weight to all chemical variables. Procrustean correlation is achieved by rotation of one data matrix (outflow chemistry through time) to match another (pore water chemistry through time), minimizing sum of squared differences between matrices. A correlation coefficient (r) is then calculated from residual sum of squares, and significance is assessed through permutation (Peres-Neto and Jackson 2001).

Fluxes, catchment budgets, and volume-weighted concentrations

Daily outflow fluxes were calculated as the product of daily volume and concentrations, infilling days without samples using the midpoint method (Eimers et al., 2008), and bulk deposition fluxes were calculated as the product of the concentration and volume collected for that time period. Fluxes were then summed to monthly and annual totals for the two sampling years, and weighted by catchment area. Annual catchment budgets were calculated from October to

September of each year by subtraction of catchment outflow from deposition inputs (note that the 2011 to 2012 budget was calculated annually to Oct. 15 due to sampling delay). Monthly volume-weighted concentrations (VWCs) in catchment outflow were calculated by dividing the total monthly flux by the total monthly volume. Full budget calculations and data are shown in Appendix A4.

Akaike Information Criteria (AIC) stepwise multiple regression models were used to explain variation of VWCs in outflow chemistry due to various biogeochemical processes. pH and SO_4 were included as indicators of SO_4-related acidification events, DOC and NH_4-N as indicators of mineralization-related events (microbial processes), and Cl as an indicator of cation exchange related to road salt inundation. These indicators were chosen based on associations in the principal components analysis (PCA) on pore water chemistry (see *Results and Discussion*). All analyses and plots were done using R 3.0.1 (R Core Team, 2013), and principal components analyses (PCA) and Procrustian randomization test (PROTEST) were performed with the 'vegan' package for R (Oksanen et al., 2013).

Results and Discussion

Current atmospheric deposition

A 95 % reduction in S emissions from smelters has been reported in Sudbury since the 1970's (Keller et al., 2007), but current deposition of SO_4 (2010 to 2011 and 2011 to 2012) is approximately one third of that reported for the area in 1977-1978 (Table 2.2). Chan et al. (1984) estimated that 25 % or less of S deposited in the region was from local smelters, and S emissions across North America have decreased comparatively less (~ 75 % lower in 2010 relative to 1980 in Canada; Environment Canada, 2012), so it is likely that a greater proportion of current SO_4

deposition is from long-range transport rather than from the local sources. Current SO_4 deposition in Sudbury is comparable to that reported over a decade ago in a catchment 250 km southeast of the Sudbury smelters where inputs are mainly from long-range sources (504 mg/m^2 SO_4-S in 2000-2001; Eimers et al., 2004). Total precipitation was also low in both study years, at about two-thirds of the values reported in 1977-1978 (Table 2.2) and below the Environment Canada climate normals for 1971 to 2000 of 899 mm. Environment Canada also reported values below climate normals for the two study years, but slightly higher than reported here (736 and 846 mm respectively; Environment Canada, 2013) (Table 2.2). These differences may be due to local weather variability, as the weather station is approximately 20 km north of the sites, but our bulk collectors may also be underreporting winter inputs because of wind-related loss of snow from open collectors.

Deposition of smelter-related metals also decreased by as much as 65 to 95 % from the 1970's in line with local emissions reductions, but current deposition is still above levels reported elsewhere (Table 2.2). This suggests that in contrast to SO_4, current inputs of Cu, Fe, Ni, Zn (and Co) are primarily from the local smelters. Metal deposition was still higher than the majority of reported values in North America in the 1970's (Galloway et al., 1982) and recent values at sites of comparable smelter proximity in Finland (Salemaa et al., 2004), and as much as 20 and 30 times above the "background" values reported for Cu and Ni in central Ontario in 2002-2003 (Landre et al., 2010) (Table 2.2). It should be noted that the emissions of metal-

Table 2.2: Annual bulk deposition of major ions (mg/m^2) and total precipitation (mm) from collectors at the six catchments for both study years. Current depositon is compared to means from two collectors on the Lohi and Clearwater Lake catchments (South) and two on the Hannah and Middle Lake catchments (Center) in 1977-1978 (from Jeffries, 1984).

	Al	Co	Cu	Fe	Mn	Ni	Zn	SO_4-S	Ca	K	Mg	Na	precip. (mm)
2010 to 2011													
C1	46.2	0.477	23.1	57.9	2.54	9.47	9.68	614	307	642	124	600	623
C2	63.2	1.05	20.8	134	7.62	8.55	8.65	490	395	642	145	279	617
BR	67.1	0.390	12.1	102	4.52	13	4.6	572	864	204	229	210	638
LU	66.8	1.08	20.2	107	28.6	24.9	10.3	470	930	345	245	350	576
D4	55.7	1.06	15.3	59.1	11.6	28.6	13.5	413	379	310	141	374	580
D5	61.8	0.744	13.4	73.1	9.17	24.8	14.5	356	835	410	136	460	581
Mean	*60.1*	*0.800*	*17.5*	*88.9*	*10.7*	*18.2*	*10.2*	*486*	*618*	*426*	*170*	*379*	*603*
2011 to 2012													
C1	15.9	0.158	10.1	27.0	4.25	6.02	6.14	349	291	223	61.3	284	600
C2	11.8	0.200	8.37	25.0	2.20	5.27	5.28	391	263	161	44.7	200	596
BR	12.3	0.109	13.2	24.2	1.96	4.21	7.22	332	281	137	46.6	188	574
LU	13.2	0.242	15.7	24.3	2.54	6.71	9.17	806	340	191	68.6	334	556
D4	17.1	0.124	6.94	21.0	2.01	3.13	4.75	421	270	160	39.9	249	607
D5	14.6	0.054	6.58	31.5	3.65	4.52	14.4	596	360	284	46.4	253	600
Mean	*14.2*	*0.148*	*10.1*	*25.5*	*2.77*	*4.98*	*7.83*	*482*	*301*	*193*	*51.3*	*251*	*589*
1977 to 1978													
South	40.6	NA	87.4	215	NA	81.6	66.7	1325	576	238	79	1127	956
Center	53.2	NA	297	402	7.67	110	48.7	1504	822	121	97	1042	917

bearing particulates from smelters in the region have decreased since the 1970's moreso than aqueous mobile forms because of modern filtration procedures (discussed in Lanteigne et al., 2012). These six sites are all within 15 km of the active smelter where particulate inputs would have been greatest (Van Alphen, 1999), and so have likely experienced greater decreases in metal deposition than wetlands further from the smelters. Metals currently deposited to these six wetlands would also be expected to be more mobile and form exchangeable bonds with organic soils (Schindler and Kamber, 2013; Lanteigne et al., 2012).

There was greater temporal variation in the deposition of smelter-related metals and SO_4 between the two study years than there was spatially among sites, with deposition two to four times higher in 2010 to 2011 compared with 2011 to 2012, largely because of elevated concentrations in the fall and winter months of 2010 to 2011 (Table 2.2, Figure 2.2). Jeffries (1984) and Freedman and Hutchinson (1980) noted similar inter-annual variation in metal deposition in Sudbury in the 1970's. This temporal variability in metal deposition tends to be high close to smelters, because particulate deposition is localized and greatly affected by climatic events (van Alphen, 1999). Between-site variation was also higher in 2010 to 2011.The bulk deposition samples that had elevated smelter-related metals in that study year were associated with high concentrations of soil-derived cations and metals (Ca, Mg, Al, Mn), suggesting that variation in 2010 to 2011 was at least in part, a result of particulate material from within watersheds (Figure 2.2). Concentrations of Ca, Mg, and Mn in these collectors was particularly high in 2010 to 2011, exceeding bulk deposition values reported in central Ontario by Watmough and Dillon (2003) and Landre et al. (2010) (Table 2.2). There were also some deposition samples that were associated with elevated Na, Cl, K, and Zn, again likely because of wind-blown materials including road-related dusts (Kelly et al., 2008; Councell et al., 2004) (Figure 2.2).

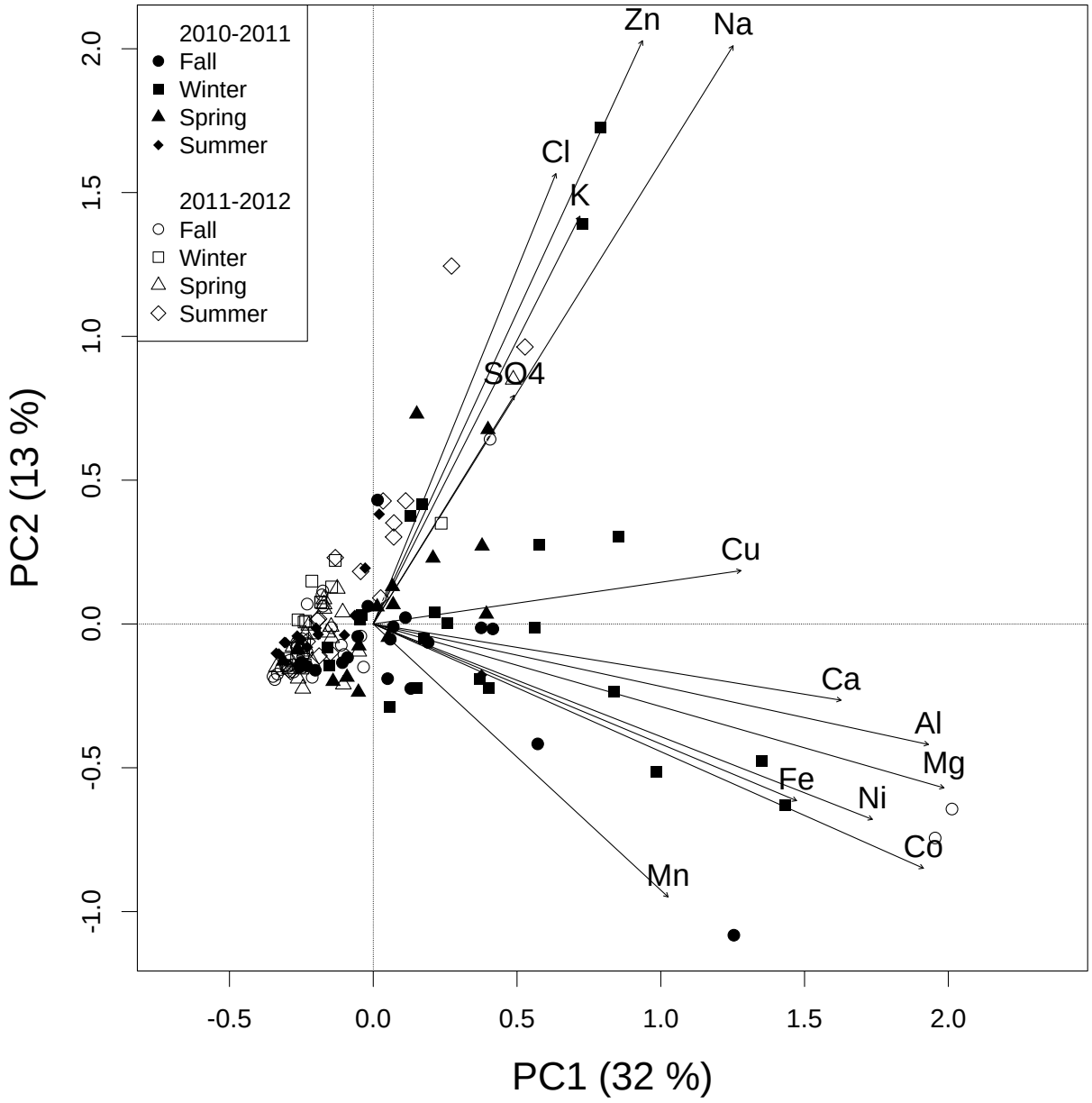

Figure 2.2: Principal components biplot of bulk deposition chemistry (metals, base cations, sulphate, and chloride) for all samples collected at the six catchments and across the two study years, with seasons indicated. The first two components are shown and collectively account for 55% of the variation in the data.

Reclamation efforts and natural recovery have resulted in substantial regrowth of vegetation in the Sudbury area since the 1970's, however much of the area is still sparsely covered and the remaining soils are heavily contaminated with smelter-derived metals in many areas (Meadows and Watmough, 2012; Nriagu et al., 1998). Annual average wind speeds have decreased substantially in response to reforestation, but these barren areas are still susceptible to high winds and frequent gusts, and averages are still slightly higher than nearby areas (Tanentzap et al., 2007). Environment Canada reported maximum winds exceeding 60 km/h in the fall months of 2010 and winter months of 2011, reaching 100 km/h in October 2010. Speeds of 100 km/h or higher in Sudbury have only been reported in two years since 1975 (Environment Canada, 2013). These winds could have resulted in higher variability in deposition due to wind-blown materials from uplands and other catchments in a landscape that is still quite barren (Figure 2.2).

Peat metal and nutrient content

All of the wetlands had high concentrations of smelter-related metals in the upper 15 cm of peat (Table 2.1), with Ni, Cu, and Co as much as 91, 126, and 6 times (respectively) above concentrations in central Ontario peatlands at sites well away from smelters (Landre et al., 2010; Adkinson et al., 2008). Peat metal concentrations in the Sudbury sites were also higher than reported in other smelter-influenced peatlands in Canada, with Ni and Cu concentrations ranging from 20 to 68 times and 4 to 11 times higher (respectively) than values reported by Kettles and Bonham-Carter (2002), but lower than smelter-impacted peatlands in Finland (e.g.: Nieminen et al., 2002).

Peat organic matter and nutrient content also varied considerably among the wetlands, factors which can affect metal behaviour. The two Daisy sites (D4 and D5) had lower C and N content,

shallow peat organic layers, and higher mineral content (Al, Fe, Mn) than the other sites. These wetlands appear to have experienced elevated inputs of upland erosional material, because the catchments are in a watershed that suffered considerable loss of upland soils and forest cover (Szkokan-Emilson et al., 2011; Dixit et al., 1996). These more barren sites also had the highest Mg and K concentrations in the peat, again indicative of inputs from erosion and leaching of mineral soils and bedrock within the catchments, or inputs of wind-blown dust (Allan et al., 1993) (Table 2.1).

Spatial and temporal variability in pore water chemistry

At all sites, 50 % or more of the variation in pore water chemistry could be explained in two principal component axes, with the first axis (30 to 37 % variation) representing a gradient of metals and cations (Co, Mn, Ni, Zn, Ca, Mg, Na) in association with SO_4 (Figure 2.3). This suggests that the release of sulphate, metals, and other cations was in response to acidification triggered by the oxidation of sulphur in peat (Eimers et al., 2007, 2003; Devito and Hill, 1999). The samples that showed this association occurred in the fall and late summer, when dry conditions or rewetting occurred (Figure 2.3). Similar oxidation-related acidification events followed by cation and SO_4 release have been widely reported following dry periods in peatlands and lake sediments (Clark et al., 2005; Tipping et al., 2003; Lucassen et al., 2002; Yan et al., 1996).

The second principal component axis represented organic matter mineralization (and possibly redox processes) and exhibited a wide gradient in NH_4 and DOC, and some metals (Al, Cu, and Fe) (Figure 2.3). Concentrations of Al, Cu, and Fe were more variable among sites than other metals, as they tend to be strongly bound to organic ligands and are more affected by differences

in organic matter content and DOC concentration (Olivie-Lauquet et al., 2001). These metals clustered intermediately between the first and second axes, suggesting both SO_4-related and mineralization-related mobilization. There was a stronger influence of SO_4 (first PCA axis) on Al, Cu, and Fe at the less-organic sites, where the influence of organic ligands would be less. Elevated NH_4 and DOC concentrations in pore water tended to occur in the spring and early summer in association with increased soil temperatures (Figure 2.3), suggesting enhanced mineralization of organic matter (to DOC) and ammonification of organic N. If conditions were reduced to the point that Mn and Fe oxides were utilized as electron acceptors, then these metals (Al, Cu, Fe) would have been released from oxides and/or from oxidized organic matter. There was also a gradient in pH along the second axis in the opposite direction of NH_4 and DOC at the organic-rich sites, suggesting that during wet conditions when mineralization was slowed, pH may have increased because of the reduction of sulphur. A release of reduced forms of metals and cations can occur during these conditions as well (Kaste et al., 2005), and this was most apparent at C2 where the SO_4-related metals were shifted slightly up the second axis and there was an association between pH, Al and Fe (Figure 2.3).

Spatial and temporal variability in stream chemistry

At all sites, wetland outflow chemistry was closely associated with chemistry of the pore water and to catchment outflow chemistry (with slight decreases in concentration observed due to additional runoff-related dilution within the outflow stream) suggesting a strong influence of the wetlands on catchment outflow chemistry (Figure 2.4). Temporal variability in catchment outflow concentrations was also consistent with the observed changes in pore water chemistry.

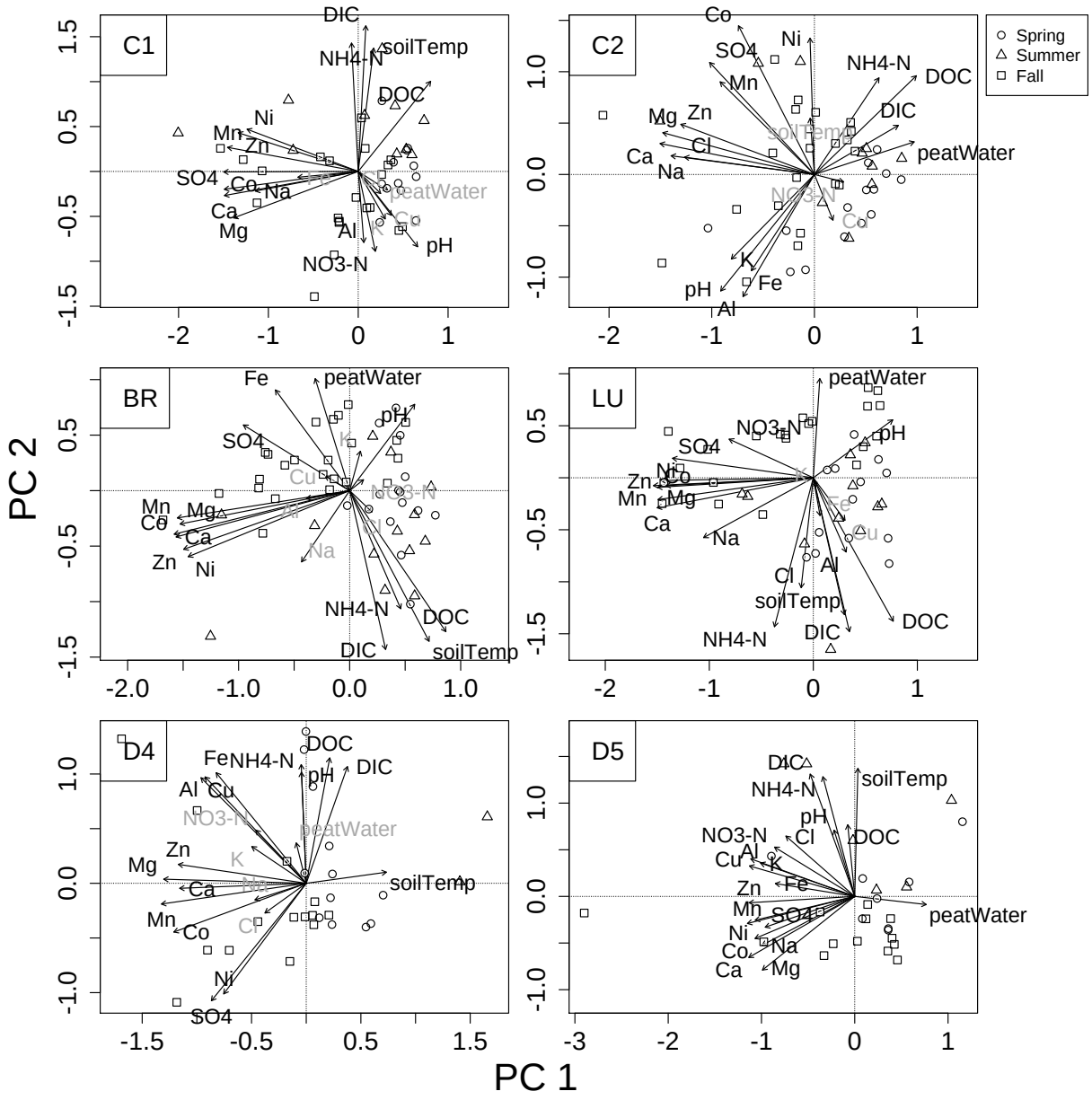

Figure 2.3: Principal components biplots of pore water chemistry in the upper 30 cm of peat (average from samples collected at 10 and 30 cm depths) from three stations in six wetlands. Associations between ions, pH, soil temperature (soilTemp), and percent water in the peat (peatWater) are shown in two components, with seasons indicated. Sample numbers differ between sites because of differences in severity and duration of dry periods when samples were unattainable. Variables loading less than 0.7 are greyed. PC1 accounted for 34, 34, 30, 45, 33 and 37 % and PC2 accounted for 17, 19, 19, 16, 13, and 17 % of the variation at C1, C2, D4, D5, BR, and LU respectively.

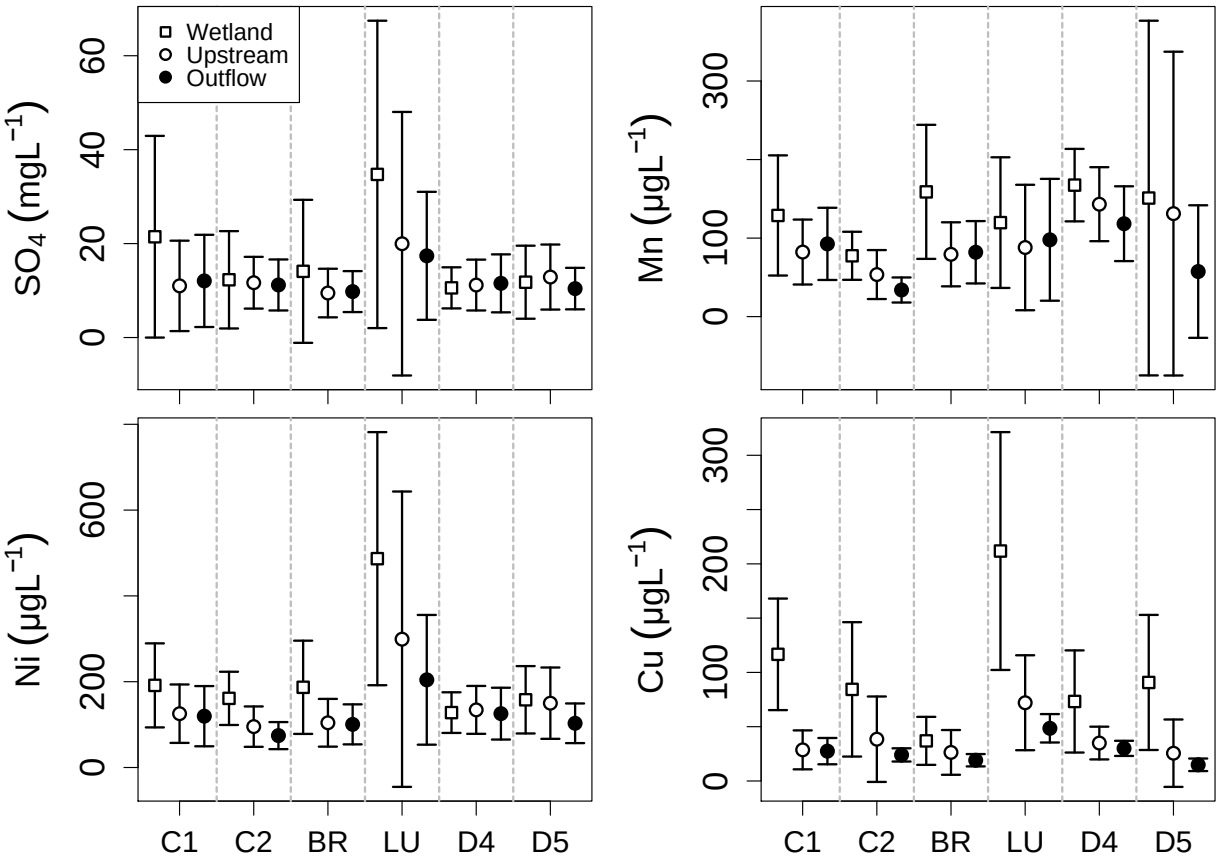

Figure 2.4: Concentrations of SO_4 and metals in wetland pore water, in the stream below the wetland (wetland outflow), and in the stream immediately above the outflow to the lake (catchment outflow). Cobalt and Zn display patterns similar to Ni, and Al and Fe display patterns similar to Cu (not shown).

Matrices of pore water and catchment outflow chemistry were significantly correlated at all sites, with Procrustes coefficients and p-values of 0.553 ($p = 0.012$), 0.746 ($p < 0.001$), 0.755 ($p = 0.001$), 0.792 ($p < 0.001$), 0.811 ($p = 0.001$), and 0.667 ($p = 0.013$) at C1, C2, D4, D5, BR, and LU respectively. The majority of variation in volume-weighted concentrations (VWCs) occurred in the fall, following a period of low water table height and stream flow. As the water tables increased and flow resumed, VWCs of SO_4 in catchment outflow increased along with VWCs of the same metals that were SO_4-related in the pore water (Co, Mn, Ni, and Zn) (Figure 2.5).

In concordance with patterns observed in the wetland pore water, the VWCs of Al, Cu, and Fe in the catchment outflow varied among sites and there was a stronger influence of DOC / mineralization events on these metals (Table 2.3, Figure 2.5). The relationship between Al, Cu, and Fe with DOC was strongest at site C1 where mean VWC of DOC in catchment outflow was highest (Figure 2.5), although DOC and/or NH_4 explained variation in these metals at all sites except C2, where road salt dusts (Cl) played a larger role and Cl concentrations were highest (Table 2.3). DOC also contributed to the variability in Co, Mn, and Ni at BR, and Mn at D5, and NH_4 explained variation in Co and Zn at D4. pH also explained variation in Fe and Mn at all sites (possibly as a surrogate of redox-related processes, as they were positively related to pH), with the exception of sites D5 and BR where DOC influence on these metals was stronger (Table 2.3).

Outflow chemistry from C1 and C2 has improved since the 1970's, with an approximately 0.2 to 0.4 unit increase in pH, and a 40 % or greater decrease in SO_4 and metal concentrations. Concentrations of Cl and Na in outflow water have also increased since the 1970's, likely because of the construction of roads in the area and more use of road salts, but

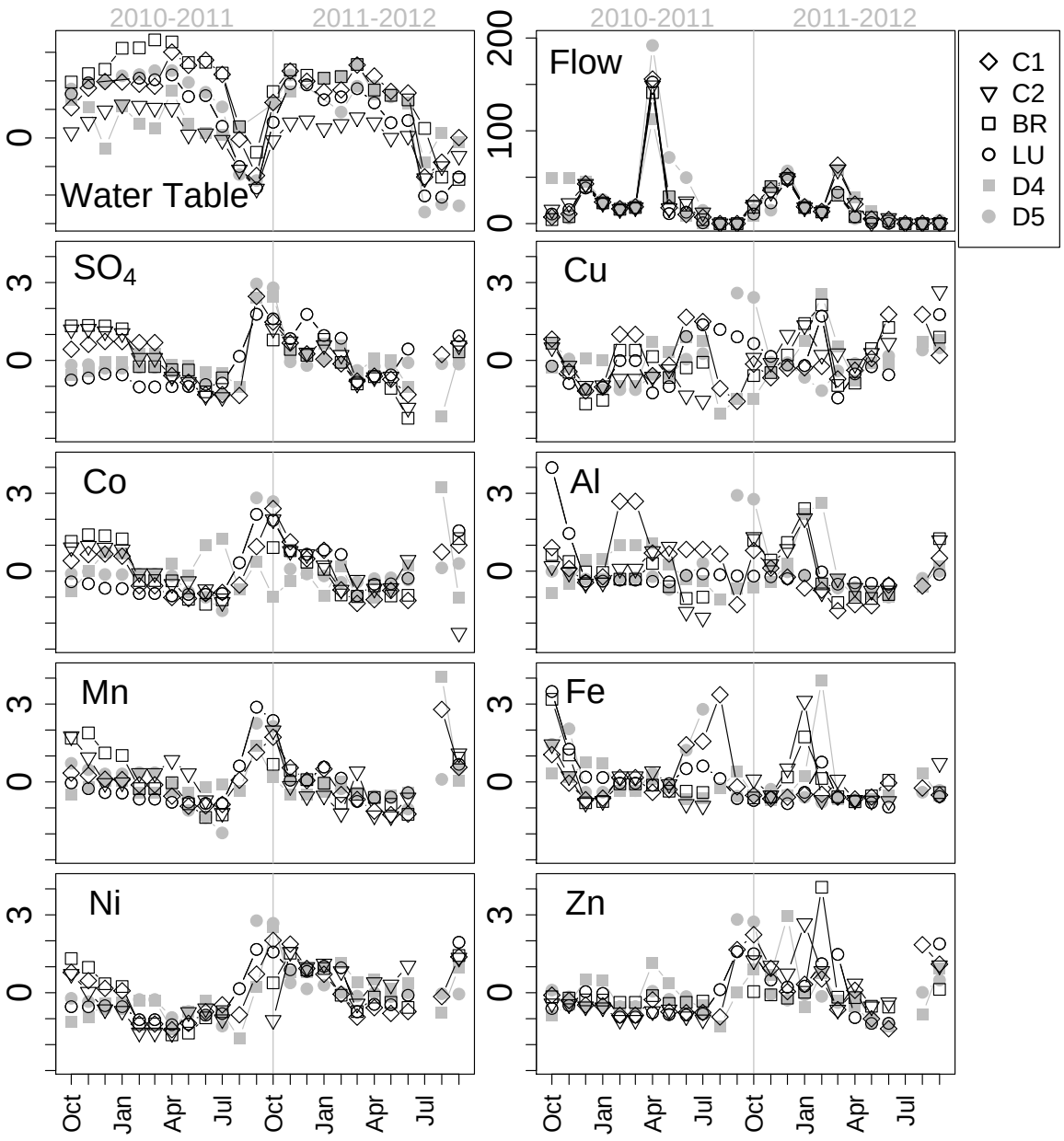

Figure 2.5: Monthly mean wetland water table height (mm), stream flow (mm), and z-scores of volume-weighted monthly concentrations of metal cations in the outflow of the six study catchments. The cut-off between the 2010 to 2011 and 2011 to 2012 sample years is indicated.

Table 2.3: Results of best-fit regression models predicting monthly volume-weighted concentration of metals with pH, SO_4, DOC, NH_4-N, and Cl, as selected by Akaike information criterion (AIC). Adjusted R^2 is shown in brackets for each model. Discussion of results is limited to predictor variables with p-values less than 0.05 (bolded).

	Al	Co	Cu	Fe	Mn	Ni	Zn
C1	**log(DOC) ***	**SO_4 ***	**log(DOC) **	**log(DOC) ***	**SO_4 ***	**SO_4 **	**SO_4 ***
	SO_4 *	*(0.629)*	-pH	**pH **	**log(Cl) ***	-pH	**log(Cl) **
	-log(Cl)		log(Cl)	**log(NH_4) **	*(0.649)*	*(0.430)*	**-pH ***
	(0.442)		-SO_4	SO_4			log(NH_4)
			(0.379)	-Cl			*(0.703)*
				(0.790)			
C2	**SO_4 **	**SO_4 ***	-Cl	**-Cl ***	SO_4	**-pH **	**SO_4 ***
	**-Cl **	-pH	SO_4	**pH ***	pH	**SO_4 ***	**-pH **
	(0.462)	Cl	-pH	log(NH_4)	-Cl	*(0.293)*	*(0.442)*
		(0.290)	log(NH_4)	*(0.336)*	log(DOC)		
			(0.410)		*(0.334)*		
BR	**SO_4 ***	**SO_4 ***	**log(DOC) ***	**log(NH_4) **	**SO_4 ***	**SO_4 ***	**SO_4 **
	log(DOC) *	**log(DOC) ***	**log(NH_4) ***	SO_4	**log(DOC) ***	**log(DOC) ***	**log(Cl) ***
	log(Cl)	-log(NH_4)	log(Cl)	*(0.345)*	-log(Cl)	**-pH **	*(0.439)*
	(0.620)	*(0.877)*	-SO_4		*(0.842)*	log(NH_4)	
			pH			log(Cl)	
			(0.376)			*(0.826)*	
LU	**log(NH_4) ***	**log(SO_4) ***	**log(SO_4) **	**log(NH_4) **	**log(SO_4) ***	**log(SO_4) ***	**log(SO_4) ***
	log(SO_4)	*(0.951)*	-log(Cl)	pH	**pH ***	log(NH_4)	-log(NH_4)
	(0.505)		*(0.246)*	-DOC	*(0.786)*	*(0.900)*	log(Cl)
				(0..536)			*(0.496)*
D4	**log(Cl) **	**log(SO_4) ***	**log(SO_4) ***	**pH ***	**log(SO_4) ***	**log(SO_4) ***	log(SO_4)
	pH	**DOC **	**log(NH_4) ***	**-log(Cl) **	**pH **	-pH	log(Cl)
	log(NH_4)	**log(NH_4) ***	*(0.441)*	**log(NH_4) ***	log(Cl)	log(NH_4)	**log(NH_4) ***
	(0.295)	pH		*(0.759)*	-DOC	*(0.873)*	pH
		(0.966)			*(0.865)*		*(0.607)*
D5	NS	NS	NS	**log(NH_4) ***	**log(DOC) **	**SO_4 ***	**log(Cl) **
				(0.169)	**log(Cl) **	**-pH **	-pH
					(0.243)	log(DOC)	*(0.404)*
						-log(NH_4)	
						(0.708)	

Dependent variables are log-transformed with the exception of: Al, Co, Zn at C1; Co, Ni, Zn at C2; Cu, Mn, Ni, Zn at D4; Ni, Zn at BR; and Zn at LU. Significance levels are indicated: *** p-value < 0.001, ** p-value < 0.01, * p-value < 0.05

export of Ca has increased less as this cation has a high affinity for organic matter and would have taken up exchange sites on peat. Despite these improvements, metal concentrations in outflow water remain high enough to potentially affect aquatic organisms (Table 2.4, Table 2.5). The mean monthly VWCs exceeded Ontario water quality objectives (PWQOs; OMOE 1999) for Al, Co, Cu, and Ni, with maximums as much as 218, 31, 15, and 21 times above the PWQOs respectively (Table 2.4). There is no PWQO established for Mn, however all values were comparable to that reported in Central Ontario with the exception of higher values at LU (Adkinson et al. 2008). Mean monthly VWCs of Fe and Zn were not above the PWQOs at any sites, but maximum concentrations exceeded the provincial guideline levels by as much as 12 and 7 times respectively (Table 2.4). It is worth noting that the concentration estimates are conservative because of the effect of the volume-weighting calculation, which down-weights the highest measured concentrations.

The potential for impacts and the degree of risk associated with these concentrations is uncertain, however free ions are generally considered to be most bioavailable geochemical species of metal and this form would be favoured in the acidic conditions brought about by SO_4-related release. Acidification would also result in elevated proton concentrations and these have the potential to reduce toxicity through competitive interactions at the site of toxicity (i.e. the biotic ligand; Paquin et al., 2002). None-the-less, the mobilization of metals, their elevated concentrations, relatively low DOC concentrations, and water chemistry changes can be interpreted as increasing the risk of toxic effects to aquatic organisms in the receiving environment, particularly in years with large water table fluctuations and low minimum water table heights.

Table 2.4: Mean (SD) volume-weighted monthly concentrations of metals in the outflows from the six catchments over two study years. Maximum monthly values are shown for each study year. 1977-1979 means are from Jeffries et al. (1984).

			Al (ug/L)	Co (ug/L)	Cu (ug/L)	Fe (mg/L)	Mn (ug/L)	Ni (ug/L)	Zn (ug/L)
C1	2010-2011	Mean	291 (76.9)	5.62 (2.31)	24.6 (11.2)	1.13 (1.11)	86.0 (26.2)	97.8 (43.5)	10.9 (7.70)
		Max.	460	8.85	41.7	3.7	138	158	32.4
	2011-2012	Mean	215 (57.4)	6.49 (3.54)	26.5 (8.44)	0.269 (0.167)	96.3 (52.5)	134 (59.1)	18.7 (12.0)
		Max.	315	13.2	42.7	0.667	205	224	38.6
	1977-1979	*Mean*	*307*	*NA*	*33*	*0.395*	*169*	*215*	*287*
C2	2010-2011	Mean	229 (82.0)	3.39 (1.13)	19.2 (4.15)	0.304 (0.178)	36.3 (12.4)	50.4 (20.3)	18.1 (3.40)
		Max.	334	4.6	27.2	0.659	57.3	90	22.1
	2011-2012	Mean	273 (91.5)	3.18 (1.59)	28.1 (5.70)	0.358 (0.269)	29.8 (15.2)	86.9 (23.2)	36.8 (14.0)
		Max.	431	5.98	41.6	1.04	60.4	114	65.3
	1977-1979	*Mean*	*521*	*NA*	*41*	*0.232*	*222*	*287*	*81*
BR	2010-2011	Mean	272 (64.7)	6.80 (3.25)	17.1 (4.72)	0.325 (0.363)	90.9 (47.0)	86.4 (45.1)	8.67 (3.27)
		Max.	362	10.4	23.3	1.2	154	155	14
	2011-2012	Mean	312 (138)	6.23 (2.44)	21.5 (6.28)	0.242 (0.214)	75.5 (27.1)	114 (33.9)	25.5 (42.9)
		Max.	554	10	32	0.781	117	163	146
LU	2010-2011	Mean	684 (934)	7.12 (6.65)	49.8 (13.0)	0.542 (0.327)	103 (100)	144 (124)	11.9 (10.3)
		Max.	3270	25.5	68.5	1.43	380	472	38.5
	2011-2012	Mean	294 (120)	12.8 (6.79)	52.5 (12.7)	0.233 (0.144)	130 (84.8)	302 (140)	21.5 (16.1)
		Max.	477	23.9	73.5	0.621	333	514	42.7
D4	2010-2011	Mean	409 (195)	9.47 (7.05)	30.0 (9.65)	0.234 (0.197)	127 (66.4)	107 (82.4)	11.0 (8.77)
		Max.	946	27.5	52.8	0.596	252	331	35.1
	2011-2012	Mean	370 (194)	10.8 (5.43)	31.5 (7.70)	0.045 (0.026)	128 (45.8)	150 (58.9)	10.9 (8.77)
		Max.	917	26.6	51.4	0.089	245	324	34.3
D5	2010-2011	Mean	159 (78.0)	2.02 (1.03)	14.4 (5.18)	0.431 (0.232)	43.9 (39.0)	67.3 (26.4)	7.85 (4.72)
		Max.	278	3.61	20.3	0.77	154	111	16.4
	2011-2012	Mean	169 (134)	1.31 (1.98)	16.6 (5.78)	0.392 (0.646)	57.8 (100)	134 (37.3)	9.69 (8.31)
		Max.	448	6.8	29.5	2.27	354	219	28.4

Table 2.5: Mean (SD) volume-weighted monthly concentrations of sulphate, hydrogen ions (as pH), DOC, ammonium, chloride, and base cations in the outflows from the catchments over two study years. Wetland water table heights (from daily data) are shown relative to soil surface. Maximum values are shown for each study year with the exception of pH and water table heights where minimums are shown. 1977-1979 means are from Jeffries et al. (1984).

			SO_4-S (mg/L)	pH	DOC (mg/L)	NH_4-N (ug/L)	Cl (mg/L)	Ca (mg/L)	Na (mg/L)	Water Table (cm)
C1	2010-2011	Mean	4.21 (3.40)	5.06 (0.303)	10.3 (6.37)	77.9 (91.5)	1.27 (0.383)	2.79 (1.73)	1.55 (0.549)	5.98 (13.5)
		Max.	11.1	4.62	24.3	264	2.3	7.16	3.12	-41.4
	2011-2012	Mean	4.07 (2.28)	4.50 (0.456)	6.47 (2.33)	64.9 (31.4)	1.85 (1.94)	3.65 (2.53)	2.23 (1.80)	1.96 (14.6)
		Max.	8.31	3.61	11.8	115	7.53	10.0	7.57	-50.3
	1977-1979	*Mean*	5.47	4.5	NA	22	0.5	3.5	1.1	NA
C2	2010-2011	Mean	3.91 (2.12)	5.06 (0.250)	7.25 (1.57)	62.2 (82.7)	36.4 (6.62)	9.87 (3.68)	9.26 (2.08)	-7.55 (10.3)
		Max.	6.11	4.73	10.2	264	43.8	13.8	11.7	-52.8
	2011-2012	Mean	3.77 (1.74)	4.53 (0.371)	8.15 (2.36)	44.2 (20.5)	29.8 (7.23)	11.4 (2.67)	9.52 (1.70)	-8.88 (6.99)
		Max.	6.14	3.7	13.6	77.2	42.2	14.3	11.8	-35.4
	1977-1979	*Mean*	5.97	4.4	NA	17	23.2	12.2	4.1	NA
BR	2010-2011	Mean	3.77 (1.41)	4.88 (0.257)	3.43 (0.773)	66.9 (78.9)	1.08 (0.688)	2.48 (1.08)	1.06 (0.214)	12.6 (12.7)
		Max.	5.24	4.4	4.24	260	1.58	3.75	1.44	-27.1
	2011-2012	Mean	3.07 (1.33)	4.42 (0.342)	4.97 (1.60)	53.3 (29.8)	1.02 (0.420)	2.42 (0.850)	1.23 (0.216)	3.36 (12.0)
		Max.	4.51	4.11	8.6	104	2.62	3.83	1.57	-29.3
LU	2010-2011	Mean	4.07 (3.84)	4.79 (0.270)	5.04 (1.34)	134 (166)	1.87 (1.52)	3.79 (2.96)	3.31 (4.42)	-1.25 (15.0)
		Max.	14.6	4.46	7.56	592	4.65	11.3	12.4	-45.4
	2011-2012	Mean	8.85 (4.27)	4.25 (0.142)	5.12 (3.17)	48.4 (23.7)	1.03 (0.458)	6.26 (2.81)	1.30 (0.299)	-6.87 (16.5)
		Max.	14.6	4.01		80.5	1.7	10.7	1.75	-53.0
D4	2010-2011	Mean	3.77 (3.14)	4.60 (0.145)	2.58 (0.637)	87.5 (105)	0.729 (0.415)	1.95 (1.26)	1.11 (0.402)	3.29 (14.5)
		Max.	12.3	4.41	3.79	313	1.71	5.34	2.05	-34.0
	2011-2012	Mean	4.47 (2.47)	4.17 (0.263)	2.31 (0.925)	36.6 (21.6)	0.834 (0.372)	1.96 (1.09)	1.33 (0.252)	-6.47 (22.1)
		Max.	11.9	3.78	3.3	95.8	1.68	5.17	2.00	-57.5
D5	2010-2011	Mean	3.54 (1.23)	5.46 (0.364)	2.96 (1.20)	129 (118)	1.28 (0.608)	2.50 (1.21)	1.28 (0.368)	-3.69 (7.58)
		Max.	6.98	5.02	4.54	324	2.48	4.6	2.08	-15.0
	2011-2012	Mean	3.74 (1.55)	4.71 (0.215)	3.15 (1.11)	40.9 (17.0)	1.75 (1.34)	3.64 (1.75)	1.91 (0.656)	1.34 (12.4)
		Max.	7.01	4.22	5.36	67.1	4.75	8.05	3.74	-34.8

Catchment budgets

Annual catchment budgets (mg/m^2/year) revealed a net loss of SO_4 from all six catchments (Table 2.6), although current deposition may actually be higher than reported because bulk collectors tend to underestimate dry deposition of SO_4 (Driscoll et al., 1998; Eimers et al., 2004). The majority of SO_4 export in 2010 to 2011 occurred during the spring flows, whereas in 2011 to 2012 SO_4 export was greatest in the fall (Oct. to Dec.), with total fall export ranging from 45 to 68 % of annual amounts (Figure 2.6). The magnitude of net loss (inputs – outputs) varied among sites and between study years, but was always ~ 50 % lower than values observed in the Sudbury area in the late 1970's (sites C1 and C2; Table 2.6).

There was a net loss of most metals (Al, Co, Mn, Ni), but considerable variation was observed between years, and among sites particularly in 2010 to 2011 when inputs appear to have been affected by wind-blown particulates (Table 2.6). These wind-blown inputs are considered a natural cause of catchment budget variability in the area, as much of the elevated inputs could have come from neighboring catchments and barren uplands, however external sources are difficult to separate from internal ones. Elevated VWCs of several cations were noted in catchment outflow during this period (Figure 2.5), and similarly high inter-annual variability in catchment budgets was also noted in the 1970's (Table 2.6). Fe budgets were variable across sites and years, with retention at C2 and BR in the first year and D4 the second study year. Fe has a relatively high affinity for organic matter and is emitted from the smelters, but there are also internal weathering sources of Fe within the catchments, and the interplay between these factors may be the cause of this variability. There was net retention of Cu at all catchments in both study years and there was only a net loss of Zn from C2 in 2011-2012 (Table 2.6). Although

Table 2.6: Annual mass balances of metals, sulphate, and other cations in the six catchments for both study years, compared to 1977-1978 and 1978-1979 mass balances at the C1 and C2 catchments.

	2010 to 2011						2011 to 2012						1977 to 1978		1978 to 1979	
	C1	C2	BR	LU	D4	D5	C1	C2	BR	LU	D4	D5	C1	C2	C1	C2
Metals and Sulphate (mg/m^2/year)																
Al	-47.7	-25.2	-20.4	-53.4	-95.0	-8.85	-34.3	-52.4	-50.6	-34.5	-53.7	-26.0	-113	-294	-163	-233
Co	-0.917	-0.015	-1.49	-0.052	-2.44	0.093	-1.36	-0.601	-1.14	-1.79	-1.80	-0.119	NA	NA	NA	NA
Cu	16.3	14.3	6.8	8.63	3.58	7.77	4.85	2.17	9.53	7.78	1.45	2.73	66.6	61.1	-11.1	-13.7
Fe	-91.7	20.8	36.9	-23.5	-24.2	-103	-19.1	-61.2	-22.3	-12.0	12.4	-30.7	-81.6	90.3	-171	-103
Mn	-21.0	-5.54	-21.1	12.1	-38.3	-1.58	-17.3	-5.05	-13.3	-17.2	-22.2	-1.31	-83.7	-120	-101	-118
Ni	-11.3	-4.82	-4.90	4.77	-4.17	4.46	-27.3	-13.8	-18.7	-41.8	-24.1	-27.9	-31.5	-94	-131	-140
Zn	6.55	2.60	1.5	7.97	9.28	10.9	1.98	-2.90	3.11	5.01	2.68	11.4	55.1	18.5	9.63	-13.4
SO_4-S	-523	-728	-451	-191	-864	-818	-648	-496	-313	-759	-357	-334	-1499	-1859	-2370	-2263
Other Cations (mg/m^2/year)																
Ca	-343	-2560	175	186	-345	-198	-437	-2153	-208	-670	-93	-572	-1240	-6270	-1690	-5650
K	472	326	43.2	183	82.3	187	86.2	-73.7	55.5	143	92.3	168	-1.82	-140	-198	-303
Mg	-107	-275	24.2	123	-215	-286	-202	-315	-114	-132	-137	-239	-392	-966	-475	-849
Na	210	-2631	-122	-661	-107	-24.7	-104	-1829	-51	131	10	-146	513	-1460	-186	-1690
Annual Runoff																
mm	307	335	301	293	450	350	240	228	186	159	179	241	443	408	685	673

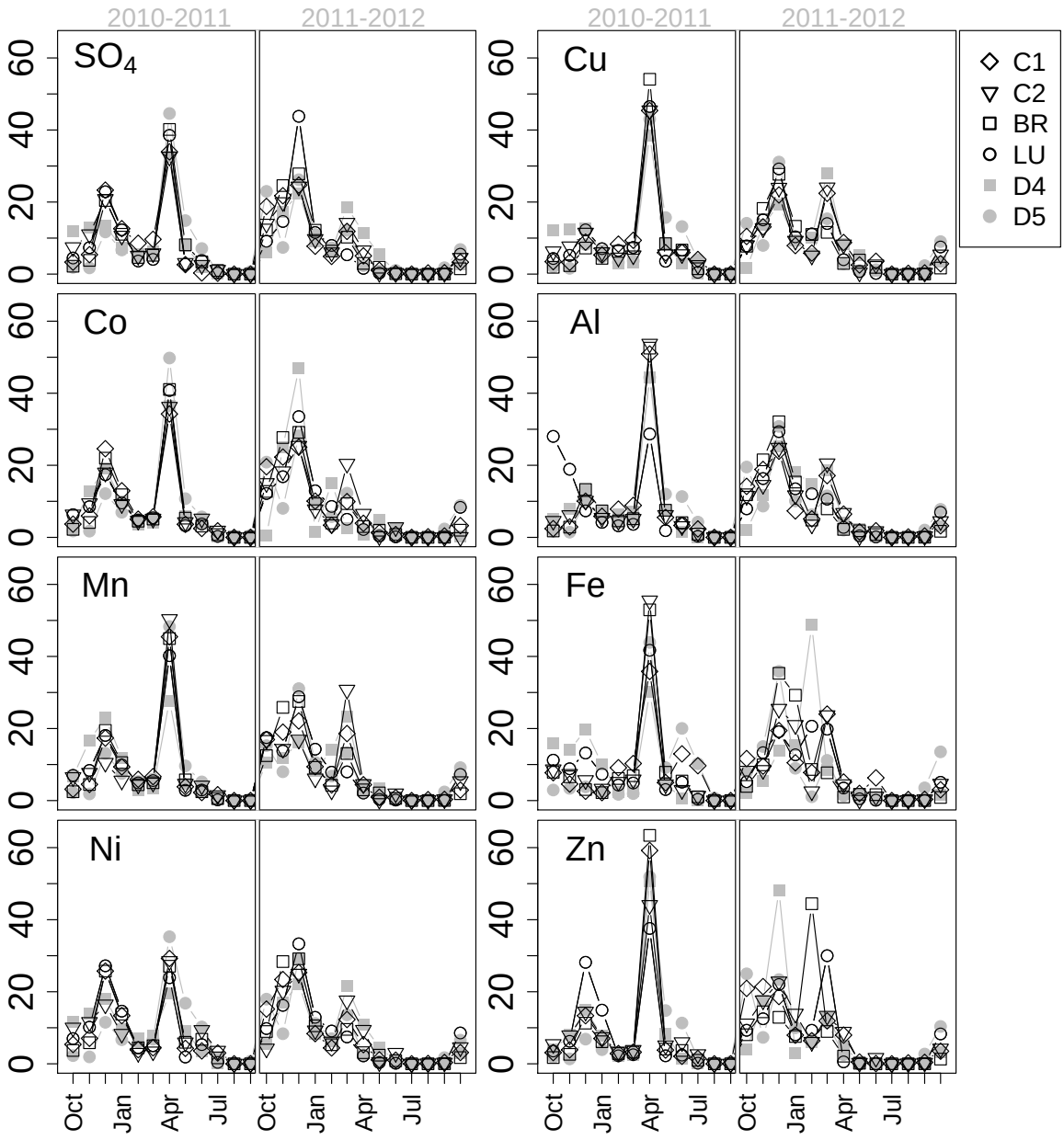

Figure 2.6: Monthly export of sulphate and metals as a percentage of total annual export from each catchment, from October to September in 2010 to 2011 and 2011 to 2012.

Cu and Zn are smelter-related metals, Cu in particular has a high affinity for organic ligands and Zn has also been shown to associate strongly with peat (Martinez et al., 1999; Novak et al., 2011). Both metals are largely retained in organic soils, with their mobilization controlled primarily by the release of dissolved organic ligands (Olivie-Lauquet et al., 2001; Spinti et al., 1995).

The spring flush in 2010 to 2011 contributed 20 to 64 % of the metal export from the sites, but in 2011 to 2012 higher concentrations in the fall played a large role in the release of metals from these catchments. Of the smelter-related metals, Co and Ni concentrations in particular were elevated in response to sulphate-mediated acidification. Export of Co and Ni in the fall (Oct. to Dec.) of the 2011 to 2012 study year ranged from 57 to 72 % and 45 to 66 % of the annual total respectively (Figure 2.6). The net loss of catchment-derived metals (Al, Mn) and cations (Ca, Mg, Na) was presumably a result of weathering and erosion, although VWCs of these catchment-derived ions were often elevated in association with sulphate as well. The release of Ca, Mg, and other cations following SO_4-related acidification has been documented elsewhere (McLaughlin and Webster, 2010). The export of Al and Mn In the fall (Oct. to Dec.) of 2011 to 2012 represented between 39 to 65 % and 38 to 66 % of the annual total respectively (Figure 2.6). The net loss of metals from the less organic wetlands was also primarily driven by SO_4-related release. Site D4 experienced high metal concentrations in the fall and consistently had the highest net-export of Al, Co and Mn and lowest net-retention of Cu. Site D5 and C2 were similar, with the lowest metal concentrations in response to SO_4 (Table 2.4), and lowest net loss of some metals and higher retention in of other metals (Table 2.6). The mineralization-related increase in metal concentrations in the summer did not play a major role in export, as flow was

low during this period. However, some of the metals released to porewater during the summer would have been flushed in the fall as well.

The net loss of metals from catchments C1 and C2 followed the same general pattern as in the 1970's but values were lower by 80 % in many cases. There has been a general increase in pH, which would result in less cation exchange and therefore lower metal concentrations, however the decrease in net loss of metals was also greater than would be expected with the approximately 40 % decrease in annual average metal concentrations in outflow streams. This discrepancy can be explained by the observed 65 % lower annual runoff out of catchments C1 and C2 than reported in the 1970's (Table 2.6). The lower annual runoff may be in response to the dry conditions during this study but also likely because of the recovery-related regrowth of forest in the area (Tanentzap et al., 2007) and the associated loss of water to evapotranspiration.

Although there has been a decrease in the net loss of metals, the export (total loss) of these metals has decreased comparatively less than deposition inputs, and exports now represent a significant source of contaminants to receiving lakes which is far greater than atmospheric inputs in some cases. For example, inputs of Co and Ni to Clearwater Lake in 2011 to 2012 were 1.79 and 35.9 mg/m^2 (12 and 7.2 times atmospheric inputs, weighted per lake area) respectively from the C1 catchment, which accounts for 24 % of the 416 ha watershed (including the lake). C2 contributed additional inputs of 0.217 and 4.99 mg/m^2 (1.5 and 1.0 times atmospheric) respectively, with a catchment area that is 6.6 % of the watershed (Table 2.1). Comparatively, the C1 and C2 wetlands contributed 41.4 and 34.0 mg/m^2 of Ni to the lake in 1977-1978, or 0.51 and 0.42 times atmospheric inputs at that time. Similar responses were observed in the catchments with less organic wetlands, with export of Co and Ni from D4 (10 % of the 312 ha Daisy Lake watershed) equating to 1.60 mg/m^2 Co and 21.3 mg/m^2 Ni to Daisy Lake, 10 and 4.3

times above mean atmospheric inputs in 2011 to 2012, respectively (Table 2.1, Table 2.2). Even site D5, which did not respond as strongly to SO_4, was a source of an additional 0.095 mg/m^2 Co and 22.3 mg/m^2 Ni (0.64 and 4.5 times atmospheric inputs respectively) at 9.4 % of the watershed area. While these wetlands have provided a valuable service of decades of metal retention, the current export of metals poses a considerable threat to lakes in smelter-impacted areas. In the early decades of smelting activity these wetlands reduced metal exports to lakes and accumulated high concentrations of metals. However, this has simply delayed the release of metals, and we are now seeing the cost of this important ecosystem service as the releases are now higher than current emissions. Although these lakes are not fed entirely by wetlands, many of them have several wetland-influenced catchments, and this study has shown that even a single catchment with a relatively small wetland can be a source of metals greater than current atmospheric inputs to lakes.

Conclusion

After the massive investment in smelter emissions reductions (>95 %), the deposition of smelter-related metals has declined in the region but aerial metal deposition into the catchments was still higher (as much as 20 and 30 times for Cu and Ni) than comparable areas further from smelters (Q1). Wetlands in this area are heavily contaminated with several metals from decades of retaining aerially deposited metals, and SO_4-related acidification events following dry periods play a large role in the release of most of these metals into pore water and stream outflow (Q2). The chemistry of the pore water is strongly related to stream chemistry and export to lakes (Q3) and smelter-related metal concentrations in streams entering the lakes exceeded water quality guidelines by as much as 20 to 30 times in some cases. As these wetlands have created a slow regulated release, the export of metals decreased comparatively less than inputs since the 1970's

and catchments containing wetlands are now a major source of several metals to lakes at a rate as much as 10 to 12 times greater than atmospheric deposition (Q4). Despite large differences in peat chemistry among sites, there were similarities among catchments with respect to processes controlling metal behaviour. Wetlands offer the immediate benefit of regulating water quality, but the potential release of these metals long after emissions reductions have been implemented must be taken into account when considering the use of wetlands for water quality regulation. This is of particular concern under dry conditions when water table decline can promote the oxidation of metals, in boreal regions affected by smelter emissions and/or mining-related effluents.

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Chapter 3. Drought-induced release of metals from wetlands in watersheds recovering from historical metal and sulphur deposition[2]

Abstract

Climate change is predicted to cause an increase in frequency and severity of droughts in the boreal ecozone, which result in the lowering of water tables and subsequent release of acidic, metal-contaminated waters from wetlands. In areas where historical deposition of metals and sulphur was severe, these episodic pulses of metals could still be reaching concentrations sufficiently high to severely affect aquatic communities in receiving waters and cause a delay in biological recovery. The objective of this study is to evaluate the impact of drought on the chemistry of stream outflow from two Sudbury wetlands with widely contrasting organic matter content to determine the response of stream water chemistry to water table decline from wetland types in the region. Stream samples were collected using ISCO^{TM} automated water collectors from June to November 2011. Following a period of drought, there was a decline in pH and a large increase in concentrations of sulphate and metal ions (Al, Co, Cu, Fe, Mn, Ni, and Zn) in water draining both peatlands, with extreme concentrations occurring over a period of about two weeks. At the site with the higher peat organic matter content there was an increase in metals that have a high affinity to bind to DOC (Al, Cu, and Fe) during the onset of drought. This study demonstrates a dramatic response to drought at two sites that differ in metal and nutrient pool

[2] Szkokan-Emilson, E.J., Watmough, S., Gunn, J.M., Kielstra, B. 2013. Biogeochemistry 116, 131-145.

sizes, hydrology, and topography, suggesting the potential for a majority of wetlands in the region to experience this response. Efforts to restore aquatic ecosystems and protect freshwater resources must take into account these processes, as disruptions to biogeochemical cycles are likely to become more prevalent in a changing climate.

Introduction

It is well recognized that boreal peatlands play an important role in regulating atmospheric cycles, but less attention has been paid to the interaction between peatland biogeochemistry and surface water quality in a changing climate. Droughts, heavy rainfall, and other extreme weather events are becoming more prevalent and the boreal ecozone may be particularly susceptible to the effects of these events (Trenberth, 2011). In northern latitudes the frequency of extreme events such as drought are expected to increase more than the changes in overall mean precipitation (IPCC 2007). Earlier peak runoff is also expected to become more common, likely leading to an increased duration of low flow and drought periods during the summer (Trenberth, 2011). If these dry periods are severe enough to result in a lowering of the water table, then the cycling of nutrients and metals can be affected and result in significant alterations to water quality in receiving waters (Macrae et al., 2012; Tipping et al., 2003; Freeman et al., 2001).

When drought conditions in a watershed results in a lowering of wetland water tables, enhanced oxic conditions develop in the peat. If these oxic conditions persist, reduced sulphur will become oxidized to sulphate and rewetting events following drought then lead to the formation of sulphuric acid (Eimers et al., 2003, 2007; Devito and Hill, 1999). Metals that are brought into solution under low pH conditions may be released into surface waters during these post-drought rewetting events. Some metals will also preferentially bind to dissolved organic ligands and form mobile organo-metal complexes, so increases in dissolved organic carbon (DOC) concentration during warm, dry summer months can result in increased mobility of metals as well (Cory et al., 2006; Antoniadis and Alloway, 2002; Olivie-Lauquet et al., 2001). The release of metals in response to water table declines has been demonstrated in wetlands elsewhere (e.g.: Landre et al.,

2009; Adkinson et al., 2008; Tipping et al., 2003), but the potential magnitude and duration of these effects in the boreal wetlands are not well understood.

The Sudbury region of Ontario, Canada has suffered nearly a century of elevated metal and sulphur (S) deposition much greater than many other parts of Ontario because of smelting activity in the area. Annual emission of sulphur dioxide (SO_2) reached a maximum of 2560 kilotonnes in 1960 and in the long term resulted in extensive contamination of soils and surface waters in the area (Keller et al., 2007; Potvin and Negusanti, 1995). Wetlands were also affected, with metal levels high enough to be toxic to plant life in some areas (Taylor and Crowder, 1983). Major reductions in atmospheric emissions of pollutants in recent decades led to a decrease in annual SO_2 emissions in Sudbury to levels below 200 kilotonnes by 2010 (OMOE, 2012). Widespread improvements in surface water chemistry have been observed, but metal and S contamination persists in many areas and biological recovery of lakes and streams has been significantly delayed (Nriagu et al., 1998; Keller et al., 2007). Nriagu et al. (1998) suggest that Sudbury catchments have been saturated to the point that it may take centuries for the flux of elevated metals and S to subside. This heavily disturbed area is also particularly susceptible to drought because of thin soils with low organic matter content and reduced vegetation cover, and it is likely that water table declines and drought-related metal releases from wetlands will be more persistent and of higher magnitude in these areas.

The effects of drought-related re-acidification of lake sediments on the chemistry and biology of Sudbury lakes has been previously demonstrated. Yan et al. (1996) found that SO_4 concentrations increased from 170 uequiv/L to 400 uequiv/L, pH decreased by 1.3 units to 4.5, and Al concentration increased approximately three-fold in a wet year following two dry years. This re-acidification event that was attributed to exposure of lake sediment to the atmosphere

resulted in a decrease in genus richness of both phytoplankton and rotifers that lasted several years (Arnott et al., 2001). This same process may occur in wetlands that are connected to recovering lakes, and the objective of this study is to evaluate the chemical changes induced by summer drought in wetland-draining catchment streams outflowing from wetlands in the Sudbury area with contrasting organic matter content. It is expected that periodic, short-term release of stored metals from wetlands will occur both during the onset of the drought (related to DOC) as well as the post-drought rewetting period (related to SO_4), and that these pulses will occur in wetlands of differing nutrient and metal content. Samples were collected from June 2011 to mid-November 2011, a year of low precipitation and above average temperatures to the point that the water tables dropped 30 cm or more below the surface and streams from these wetlands stopped flowing for approximately two months.

Methods

Site descriptions and peat samples

A preliminary survey of vegetation and annual water table fluctuation in 29 wetlands was conducted in the region in 2010 (Appendix A1), and peat samples were collected from a subset of 18 wetlands (primarily poor or transitional fens) revealing a range in peat C content from 16.7 % to 49.9 % (mean 40 %, SD 7.9 %) and S ranging from 0.3 % to 1.2% (mean 0.71 %, SD 0.24 %) (See Appendix A1). Two wetlands from the survey were then selected to be representative of the range in organic matter content with metal and nutrient content at the low-ends and high-ends of concentrations observed regionally, and that were within the city limits of Greater Sudbury and drain into lakes. One of the wetlands drains into Lake Laurentian (LU) and the other drains into Daisy Lake (D4). LU is a 2.29 ha poor fen peatland within an 11.0 ha catchment

(46º27'17.81" N, 80º58'0.96" W). This site is 7.3 km from an active Cu-Ni smelter, and has experienced a moderate loss of vegetation due to emissions from historic smelting practices. In contrast, D4 is a 0.45 ha wet meadow within a 32.4 ha catchment (46º27'17.71" N, $80^0$52'55.29" W). This site is 13.6 km from the active smelter, and is in an area with heavy loss of upland vegetation from historical smelting practices and erosion of upland mineral soil, which likely contributes to the higher mineral content of the peat (Figure 3.1, Table 3.1). LU has a deeper, less dense, organic-rich peat layer (>2m deep), and D4 has a thinner but denser organic layer (~30 cm) overlying a mineral substrate. A previously conducted survey of water table fluctuations in 29 Sudbury wetlands found a mean fluctuation of 24.2 cm (SD of 12.6 cm) with average minimum water table heights of 23.0 cm below soil surface (Appendix A1). Based on this finding and the observed fluctuations at the selected sites, all sampling was restricted to the upper 30 cm where biogeochemical activity and hydrologic conductivity (and therefore influence on surface water quality) should be greatest (Clymo, 1984). Peat samples were taken from five locations within each wetland at surface (within 0 to 15 cm depths) and a deeper layer (within 15 to 30 cm depths). Samples were digested with trace grade HNO_3 at 100 ºC for 8 hrs, and then diluted to 2% HNO_3. Analysis was done with a PerkinElmer Optima 7000DV ICP-OES (Al, Ca, Co, Cu, Fe, K, Mg, Mn, Ni, Zn) and an ELEMENTAR combustor for C, N, and S. NIST-1515-SRM apple leaves were included to verify accuracy and precision, and recoveries ranged from 85 to 98 %.

Stream water chemistry and bulk deposition

Stream water outflow was monitored using ISCO™ automated water collectors set to sample every eight hours from June 1, 2011 to November 11, 2011 to capture the drought and subsequent rewetting event. The drought period of this study is defined as starting on June 29th

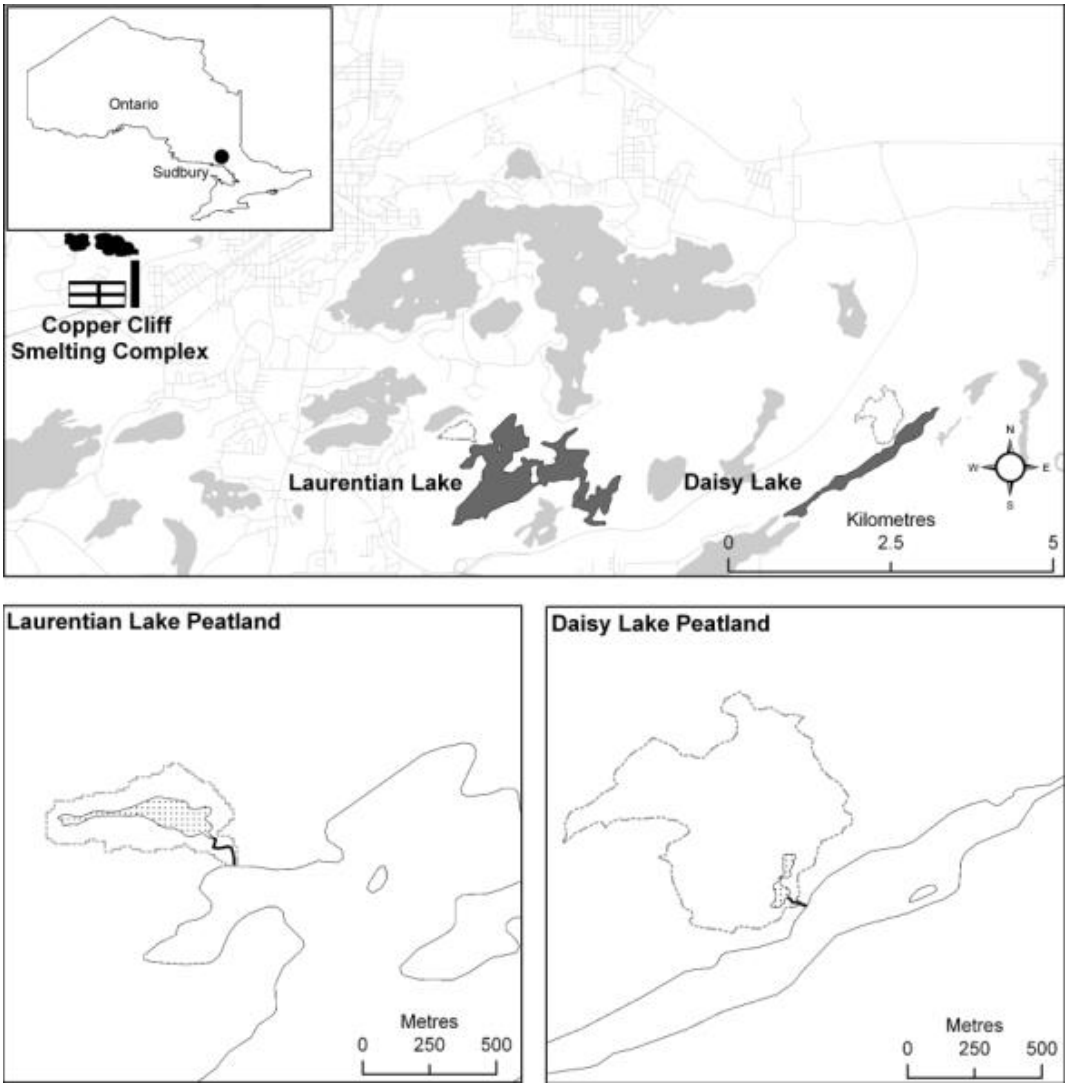

Figure 3.1: The D4 wetland is 13 km from the Copper Cliff smelter (46°27'17.71" N, 80°52'55.29" W) and drains into Daisy Lake (lower right), and the LU wetland is 7 km from the smelter (46°27'17.81" N, 80°58'0.96" W) and drains into Lake Laurentian (lower left). The two lakes are located within the city of Greater Sudbury, Ontario (upper) (Figure generated with data from Government of Canada remote sensing data).

Table 3.1: Means and standard deviations of metal, cation, and nutrient concentrations in peat from 5 locations at 15 cm depth and 30 cm depth. Total pool sizes are calculated (0 - 30 cm) as sums of the pools from each layer.

		0 - 15 cm Mean (SD)				15 - 30 cm Mean (SD)				0 - 30 cm Pool (kg/ha)	
		LU		D4		LU		D4		LU	D4
Al	(g/kg)	3.36	(0.78)	21.0	(4.50)	5.33	(0.43)	45.9	(7.55)	3460	25978
Ca	(g/kg)	5.84	(2.33)	0.72	(0.16)	10.7	(1.79)	2.59	(1.64)	6701	1349
Co	(mg/kg)	17.3	(4.35)	11.8	(1.52)	19.4	(8.14)	31.6	(6.71)	13.9	17.2
Cu	(mg/kg)	1238	(428)	711	(183)	86.4	(44.3)	160	(90.5)	349	255
Fe	(g/kg)	7.87	(0.73)	15.3	(0.81)	2.55	(0.27)	34.5	(6.36)	3207	19407
K	(g/kg)	1.02	(0.17)	1.04	(0.40)	0.09	(0.03)	3.27	(0.58)	298	1734
Mg	(g/kg)	0.40	(0.07)	1.72	(0.98)	0.72	(0.14)	7.57	(1.25)	453	3839
Mn	(mg/kg)	47.1	(13.8)	62.5	(22.6)	54.1	(11.2)	588	(286)	38.4	280
Na	(g/kg)	1.24	(0.34)	0.49	(0.19)	0.43	(0.11)	0.61	(0.04)	518	398
Ni	(mg/kg)	920	(231)	275	(47.2)	199	(71.9)	271	(148)	326	192
Zn	(mg/kg)	64.7	(20.2)	41.3	(14.0)	15.2	(9.62)	156	(26.9)	23.5	80.6
N	(%)	1.86	(0.23)	1.34	(0.21)	1.80	(0.12)	0.43	(0.11)	13487	5363
C	(%)	49.2	(0.49)	17.3	(3.40)	51.5	(0.82)	5.58	(1.44)	375923	69660
S	(%)	0.68	(0.09)	0.24	(0.07)	0.43	(0.05)	0.10	(0.02)	3783	1040
Peat	Bulk density (g/cm^3)	0.165	(0.03)	0.172	(0.06)	0.329	(0.07)	0.299	(0.06)		

when water table height and stream flow begin to drop. This captures a period of low-flow and associated chemistry changes during the onset of drought, as well as the period of zero flow starting in early August. The onset of drought is defined as the period from June 29th until flow completely ceases at each site. The rewetting period begins when stream flow returns and SO_4 concentration peaks (October 13th), ending two weeks later (October 27th) when SO_4 begins to stabilize. A bulk deposition collector was set up in each wetland one meter above the ground, and samples were retrieved every 2 to 4 weeks (depending on rain events). Samples were always collected within a few days of the first of each month to provide estimates of monthly totals. Input fluxes were calculated by multiplying the concentration of each solute in bulk collectors by the volume collected for that time period, and summed to a monthly total.

Stream water and bulk deposition samples were filtered at upon collection with 80 µm Nitex mesh and pH was measured with an Accumet model 15 pH meter. Samples were then filtered at 0.2 µm with VWR Nylon syringe filters and a portion of the sample was acidified with trace grade HNO_3 and analyzed for dissolved metals (Al, Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Zn) and base cations (Ca, K, Na, Mg) using a PerkinElmer Optima 7000DV ICP-OES. Un-acidified portions of the samples were analyzed for NH_4-N with a Bran+Luebbe AutoAnalyzer3 spectrophotometer, SO_4 and NO_3-N with a DIONEX ICS 1100 ion chromatographer, and DOC and DIC with a Shimadzu TOC-VcpH analyzer. For brevity, ions are identified without their associated charge.

Water table and stream flow

Water table height in each wetland was recorded every 15 minutes using TruTrack™ WT-HR 1000 Water Level Loggers installed in wells from 0.70 m below ground to 0.30 m above ground.

Stream water levels were recorded with HOBO™ U20 Water Level Loggers set to record every 15 minutes. Stream flow was measured across a range of water heights over two years using a Marsh-McBirney Flo-Mate™ 2000 velocity meter. Discharge for each 15 minute period was then estimated using power rating curves generated for each site from two years of flow data (collected across a range of stage heights), yielding R^2 values of 0.99 and 0.96 for LU and D4, respectively (Appendix A3). Total discharge volume (L) over 8 hours was calculated by summation of these estimates to correspond with ISCO surface water sampling periods. Chemical concentrations were converted to fluxes by multiplying the volume per 8 hour period by the mean of the concentrations at the beginning and end of that 8 hour period. These output fluxes were then summed to give totals for the entire sampling period (April to November 2011), as well as proportions of flux during the rewetting period. Proportions of fluxes during the drought were also calculated to capture the influence of chemistry changes during low-flow periods at the onset of drought.

Principal components analysis (PCA) was performed to identify and present the associations between chemical parameters in stream water through the study period. Loadings of chemical parameters on each principal component were scaled proportional to eigenvalues based on the method in the 'vegan' R package (Oksanen et al., 2012). Cadmium was excluded from principal components analyses because all values were below detection limits, and Cr and Pb were excluded because all values were below detection limits with the exception of a few points at LU in mid-summer. All analyses and plots were done using R (R Core Team, 2012).

Results

Peat metal and nutrient pools

Carbon, N, and S concentrations and pool sizes were higher at LU compared with D4 (Table 3.1). Aluminum, Fe, Mg, and Mn concentrations were higher in peat (0 to 30 cm) at D4 compared with LU, resulting in a larger pool sizes at D4 compared with LU. Cobalt and Zn concentrations were higher in the upper layer (15 cm) of LU's peat compared to D4 but higher concentrations in the deeper layer (15 to 30 cm) of D4 resulted in overall larger estimated pool sizes compared with LU. Copper and Ni concentrations were higher at LU in the upper layer and lower in the deeper layer, and estimated Cu pools were comparable between the two sites (Table 3.1).

Deposition, stream flow, and water table changes

The Sudbury area experienced a drought in late June that lasted into October of 2011. Precipitation was comparable to climate "normals" (1981-2010) in the early spring before the drought with low precipitation in March and May balanced by April and June highs. Stream water discharge and water table heights were relatively constant through May and June (Table 3.2). A high flow event occurred in mid-June at both sites and resulted in slight water table rises prior to the onset of the drought (Figure 3.2). In July, August, and September LU experienced 70.6 %, 39.7 %, and 37.3 % of the normal mean precipitation and D4 experienced 70.6 %, 25.6 %, and 19.6 % of the normal mean precipitation (Table 3.2). Temperatures were 2.2 ^{o}C, 1.0 ^{o}C, and 1.2 ^{o}C higher than normal monthly mean respectively (Environment Canada data, Table 3.2). Water tables began to drop at this time, and fell below the surface by July 8th at LU and July 17th at D4. Mean water table heights in August were 27.5 cm and 24.9 cm below surface at LU and

Table 3.2: Total monthly precipitation, discharge, and mean water table position (relative to surface) for each site and temperature for the Sudbury area compared to the monthly 'normals' (1981-2010). Environment Canada data was retrieved from the National Climate Data and Information Archive and collected at a weather station near the Sudbury Airport approximately 20 km north of the sites (46°37'32.00" N, 80°47'52.00" W) (Environment Canada, 2013).

	LU			D4			Env. Canada 2011 Data		Env. Canada 'Normals'	
Month	Mean (SD) Water Table (cm)	Precip. (mm)	Discharge (mm)	Mean (SD) Water Table (cm)	Precip. (mm)	Discharge (mm)	Precip. (mm)	Mean Temp. (°C)	Precip. (mm)	Mean (SD) Temp. (°C)
April	12.1 (1.99)	142	152	13.6 (1.51)	145	192	128	2.9	65.7	3.77 (2.08)
May	4.49 (2.61)	23.1	10.7	9.45 (1.37)	23.1	71.3	55.9	12.1	83.4	11.1 (2.05)
June	4.83 (3.14)	103	12.2	5.99 (2.51)	103	49.5	103	16.4	80.3	16.5 (1.49)
July	-5.93 (7.92)	54.3	0.82	0.88 (7.81)	54.3	14.3	26.0	21.3	76.9	19.1 (1.37)
August	-20.0 (8.14)	33.9	0.00	-22.8 (10.6)	21.9	0.98	66.3	19.0	85.4	18.0 (1.31)
September	-27.5 (14.4)	37.7	0.00	-24.9 (13.6)	19.8	0.72	63.3	14.2	101	13.0 (1.58)
October	-4.51 (13.9)	78.1	10.4	1.77 (10.5)	80.1	15.1	110	8.2	90.9	6.03 (1.50)
November	8.96 (2.07) *	55.4	21.1*	12.1 (1.54) *	67.5	12.8 *	87.4	2.0	78.5	-1.02 (2.03)

* Measured up to November 11, 2011.

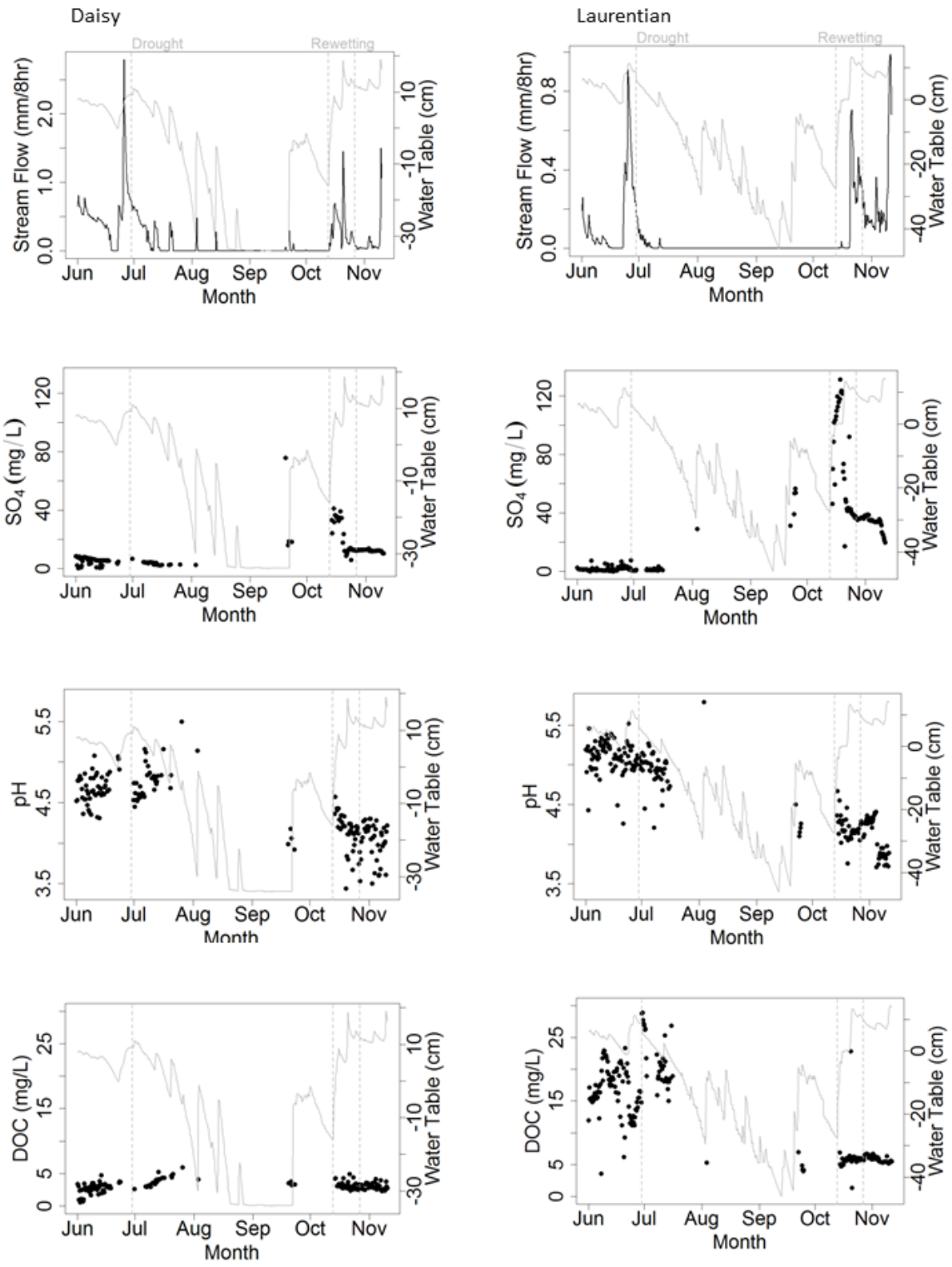

Figure 3.2: Stream flow, sulphate, pH, and DOC in the streams flowing out of the D4 and LU wetlands, from June 1 to November 11, 2011. Water table position is indicated, and the drought and rewetting periods are delineated with dashed lines. Dates are labelled at the 1st of each month.

D4 respectively. Stream flow ceased by late July with a few intermittent runoff events occurring at D4 (allowing a few samples to be collected) until the rewetting period (Figure 3.2, Table 3.2). Temperatures remained high into the fall, with October and November at 2.17ºC and 3.02ºC above the normal mean. Water tables increased at both sites in late September, and by mid-October they were above the surface. This was followed by the resumption of flow from both sites, and the beginning of the rewetting period (Figure 3.2, Table 3.2). Despite comparable precipitation inputs, bulk deposition of metals and sulphate differed between the two sites, with higher input fluxes of SO_4, Al, Fe, Zn at LU. Deposition inputs of all other metals (Co, Cu, Mn, and Ni) were higher at D4, despite being further from the active smelter (Table 3.3).

Stream water chemistry: responses to drought and rewetting

Most of the variation in stream water chemistry at both LU (54.7 %) and D4 (49.9 %) was a result of the rewetting event (first principal components, Figure 3.3, Table 3.4). During rewetting in the fall, the pH of the stream at the LU site fell to 3.76 and SO_4 reached a maximum of 131 mg/L (mean of 70.4 mg/L) (Figure 3.2, Table 3.5). Concentrations of Ca, Co, Mg, Mn, Na, Ni, and Zn in the LU stream increased during the acidification episode (Figures 3.3 and 3.4, Table 3.4 and 3.5). Most notably Ni reached a maximum of 1708 µg/L and Co reached a maximum of 63.7 µg/L (Figure 3.4, Table 3.5).

Aluminum and Cu concentrations also increased in the fall at LU, but to a much lesser extent than occurred in the early summer. Nitrate concentration increased to 1743 µg/L during the rewetting in the fall, whereas DOC and Fe concentrations decreased (Figures 3.2 and 3.4, Table

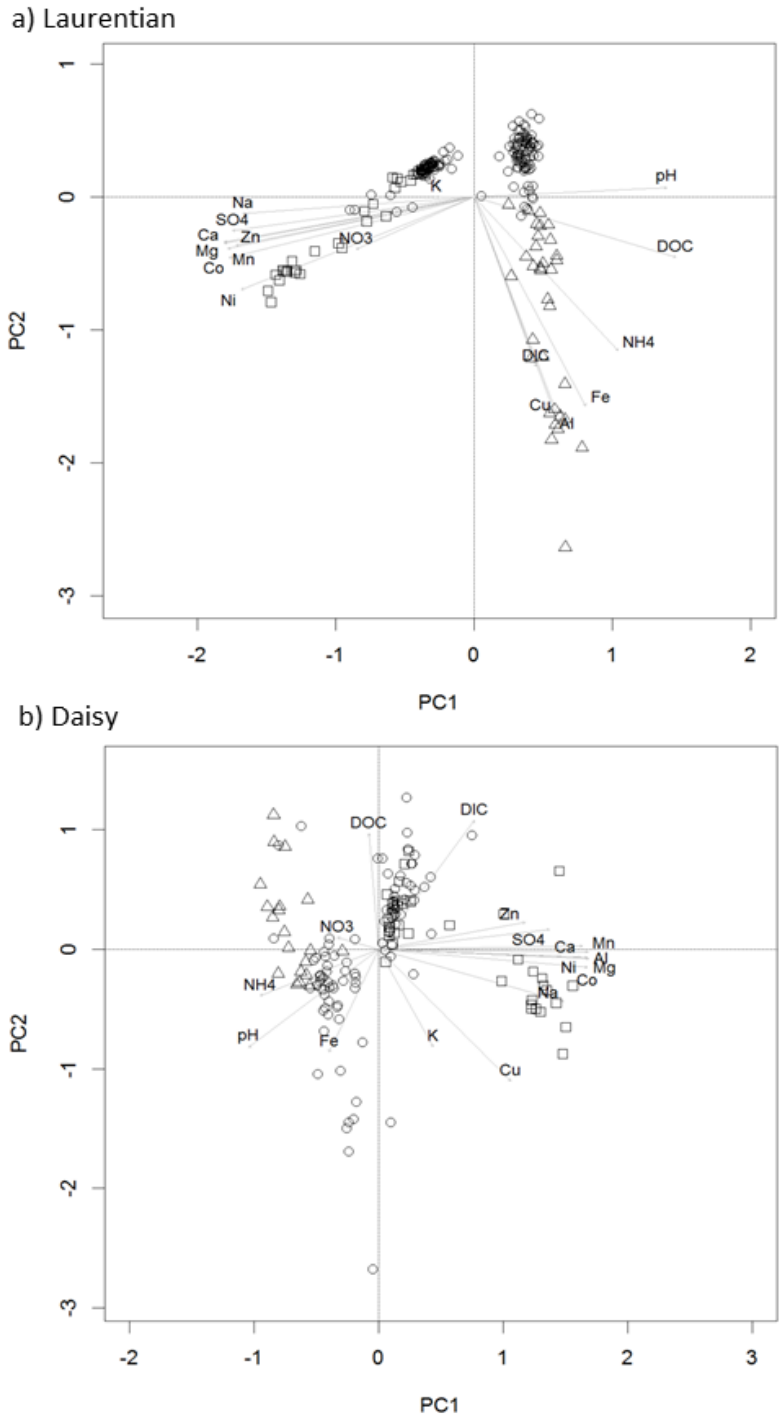

Figure 3.3: Principal components biplot of stream samples. Component 1 (PC1) explains 54.7% of the variation in LU (a) and 49.9% of the variation at D4 (b), and represents the post-drought rewetting period (squares). Component 2 (PC2) explains and additional 21.2% of the variation at LU (a) and 12.4% of the variation at D4 (b), and represents the drought period (triangles). All samples outside of the drought and rewetting periods are indicated with circles.

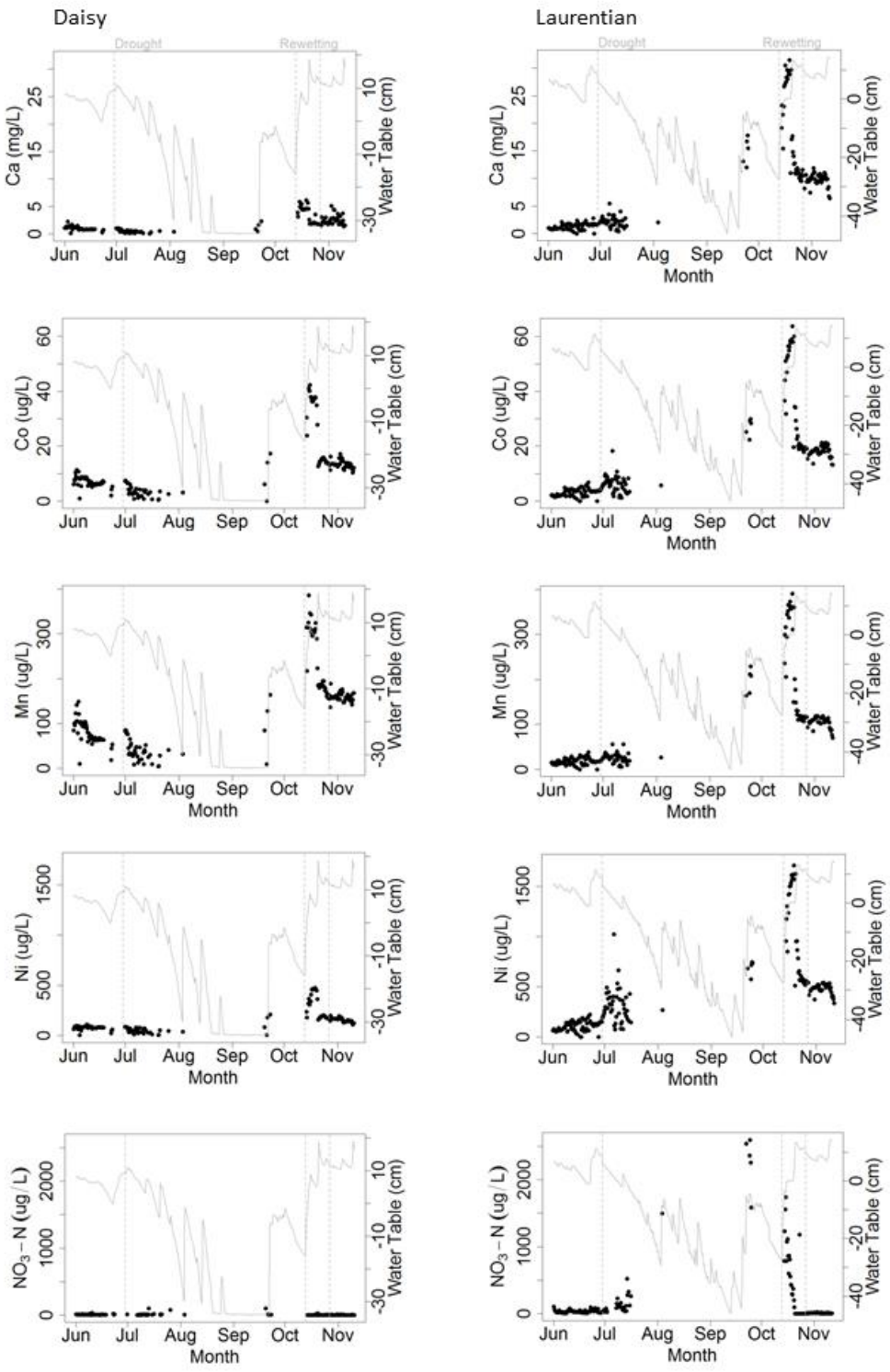

Figure 3.4: Metals, cations, and nutrients the streams flowing out of the D4 and LU wetlands that responded most dramatically to the rewetting period in October 2011. Water table position is indicated with a gray line, and the drought and rewetting periods are delineated with dashed lines. Zn, Mg, and Na responded similarly, but are not shown. Dates are labelled at the 1st of each month.

Table 3.3: Bulk deposition (input) and stream water (output) fluxes of metals and sulphate for the two wetlands during the study period (June 1 2011 to November 11 2011), and proportions of flux during the drought and the post-drought rewetting periods.

	Total Input (mg/m^2)		Total Output (mg/m^2)		Drought Output Flux (%)		Rewetting Output Flux (%)	
	LU	D4	LU	D4	LU	D4	LU	D4
Al	33.2	28.7	15.0	18.2	14.4	7.59	22.9	53.9
Co	0.40	0.85	0.46	0.53	2.11	7.46	44.7	55.5
Cu	3.26	5.07	2.31	1.21	15.9	12.0	19.5	30.2
Fe	42.1	16.9	62.6	3.19	44.5	15.3	1.80	15.8
Mn	3.69	9.13	2.41	5.63	1.57	8.01	44.6	49.7
Ni	6.85	13.1	12.5	6.01	3.47	8.52	44.6	55.6
Zn	4.58	3.31	1.11	1.30	1.36	5.22	38.3	45.5
SO_4	636	296	745	443	0.24	2.22	49.7	60.9

Table 3.4: Loadings of stream water chemistry on the first two principal components from both the LU and the D4 site. The first components represent the post-drought rewetting period, and the second components represent the drought period. Variables that are loaded at 0.6 or higher on the first two components are bolded. Loadings are proportional to eigenvalues (see Oksanen et al. 2012).

	D4		LU	
	PC1: Rewetting	PC2: Drought	PC1: Rewetting	PC2: Drought
Variance	49.9 %	12.4 %	54.7 %	21.2 %
Al	**1.675**	-0.066	0.585	**-1.628**
Ca	**1.635**	0.027	**-1.805**	-0.350
Co	**1.676**	-0.152	**-1.768**	-0.459
Cu	**1.059**	**-1.100**	0.598	**-1.629**
Fe	-0.400	**-0.857**	**0.809**	**-1.571**
K	0.435	**-0.817**	-0.272	-0.003
Mg	**1.688**	-0.082	**-1.805**	-0.342
Mn	**1.683**	-0.022	**-1.779**	-0.391
Na	**1.485**	-0.436	**-1.671**	-0.124
Ni	**1.628**	-0.067	**-1.682**	**-0.699**
Zn	**1.176**	0.223	**-1.722**	-0.366
DIC	**0.768**	**1.074**	0.447	**-1.276**
DOC	-0.078	**0.966**	**1.461**	-0.453
NH4-N	**-0.952**	-0.388	**1.043**	**-1.156**
NO3-N	-0.331	-0.097	**-0.851**	-0.393
SO4	**1.373**	0.164	**-1.745**	-0.253
pH	**-1.043**	**-0.822**	**1.394**	0.067

3.5). All output fluxes were less than inputs at LU except for SO_4, Cu, Fe, and Ni, with the rewetting event accounting for much of this loss (with the exception of Fe). The flux of Co, Mn, Ni, and SO_4 during this two-week event in the fall accounted for between 44 % and 50 % of the total export during the study period (June to November 2011) (Table 3.3).

Stream chemistry at D4 responded similarly to LU during the fall re-wetting period. The pH of the stream fell to 3.44 and SO_4 reached a maximum of 41.0 mg/L, but a spike in SO_4 concentration also occurred during a short event in September associated with a rainfall event. Similar to LU, large increases in Co, Mn, Ni, and Zn concentration were observed during the fall re-wetting period acid pulse at D4 (Figures 3.3 and 3.4, Table 3.4). Ni concentrations reached a maximum of 472 µg /L and Co reached 42.2 µg /L (Table 3.5). Aluminum concentration peaked at 1.30 mg/L during rewetting and Cu increased as well, but only to values that were observed in the early summer (Figure 3.5, Table 3.5). There was evidence of increases in Ca, Mg, and Na and a small increase in NO_3-N concentration during the fall re-wetting event, but the NO_3-N increase was not as clear as in LU, and no post-drought DOC decline was observed (Figure 3.2, Table 3.5). All output fluxes of metals were less than inputs at D4, but SO_4 output was greater than input and the rewetting event accounted for 60.9 % of this loss. Fluxes of Al, Co, Mn, Ni, Zn and SO_4 during this two week event accounted for between 45 % and 61 % of the total flux during the entire sampling period (Table 3.3).

The period of low-flow during the onset of drought was also responsible for a large amount of the variation in stream chemistry at LU (21.2 %) but the two sites responded quite differently with less variation explained at D4 (12.4 %) (second principal components, Figure 3.3, Table 3.3). Stream pH values were highest in the early summer and tended to decrease at LU as the

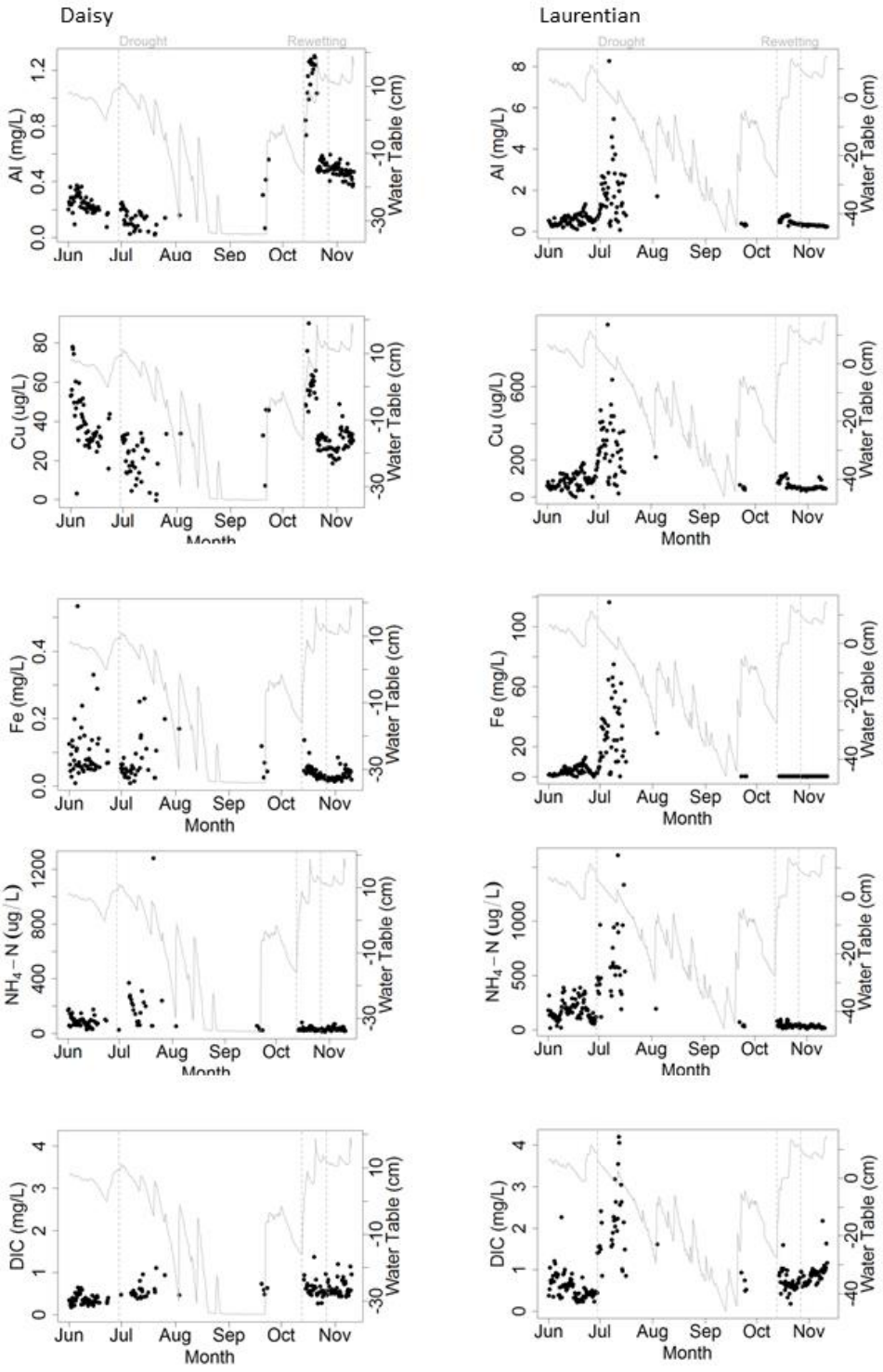

Figure 3.5: Metals, cations, and nutrients in the streams flowing out of the D4 and LU wetlands that responded most dramatically to the onset of the drought period in June and July of 2011. Water table position is indicated with a gray line, and the drought and rewetting periods are delineated with dashed lines. Dates are labelled at the 1st of each month. Note that the y-axes are scaled differently between sites to reveal patterns within sites.

Table 3.5: Concentrations of metals, nutrients, base cations, and pH (max, mean, standard deviation) in stream water from the LU and D4 wetlands during the drought and the post-drought rewetting periods.

	Drought: Maximum		Drought: Mean (SD)		Rewetting: Maximum		Rewetting: Mean (SD)	
	LU	D4	LU	D4	LU	D4	LU	D4
Al (mg/L)	8.26	0.25	1.95 (1.48)	0.13 (0.06)	0.81	1.30	0.51 (0.16)	0.81 (0.34)
Co (ug/L)	18.3	7.48	6.08 (2.95)	3.56 (1.99)	63.7	42.2	35.0 (16.8)	24.5 (11.5)
Cu (ug/L)	938	34.0	273 (163)	2.16 (9.50)	125	90.0	74.9 (27.8)	43.4 (16.6)
Fe (mg/L)	116	0.26	29.8 (23.4)	0.07 (0.06)	0.33	0.14	0.15 (0.05)	0.04 (0.02)
Mn (ug/L)	56.2	85.5	25.2 (10.4)	39.5 (23.1)	390	387	213 (109)	237 (70.8)
Ni (ug/L)	1023	86.7	308 (167)	48.4 (24.3)	1708	472	962 (442)	276 (122)
Zn (ug/L)	28.6	20.1	11.3 (5.89)	6.56 (3.98)	199	172	75.5 (39.3)	45.4 (31.2)
SO_4 (mg/L)	29.0	6.73	1.9 (4.9)	3.48 (1.03)	131	41.0	70.4 (35.0)	21.7 (11.3)
Ca (mg/L)	5.46	1.01	2.11 (0.92)	0.50 (0.28)	31.5	6.14	18.0 (7.97)	3.27 (1.52)
K (mg/L)	2.45	2.05	0.48 (0.37)	0.35 (0.32)	1.70	3.33	0.64 (0.42)	1.09 (0.64)
Mg (mg/L)	0.85	0.50	0.41 (0.15)	0.23 (0.14)	5.79	2.58	3.39 (1.43)	1.42 (0.63)
Na (mg/L)	1.28	1.23	0.57 (0.21)	0.74 (0.32)	2.39	2.53	1.70 (0.29)	1.47 (0.50)
DIC (mg/L)	4.20	1.11	2.06 (0.84)	0.58 (0.19)	1.59	1.37	0.71 (0.24)	0.61 (0.19)
DOC (mg/L)	28.9	5.95	20.9 (4.83)	3.84 (0.82)	22.8	4.89	6.10 (2.84)	3.14 (0.59)
NH_4 (ug/L)	1608	1281	589 (321)	207 (248)	95.0	81.3	43.7 (21.3)	31.8 (11.7)
NO_3 (ug/L)	1497	100	156 (263)	17.0 (27.2)	1743	26.4	763 (452)	7.14 (7.81)
pH	4.21 *	4.45 *	4.96 (0.23)	4.77 (0.23)	3.76 *	3.44 *	4.20 (0.15)	4.13 (0.25)

* Note: Minimum pH is presented.

water table dropped, whereas pH tended to increase at D4 (Figure 3.2). Aluminum Cu, and Fe concentrations were much higher at LU compared with D4 and increased during the early part of the summer at LU. Concentrations of NH_4-N and DIC also increased during the early summer (onset of drought) at LU and there was a moderate increase in NO_3-N during this period, but a peak of 1497 µg/L was not reached until later during the drought (Figure 3.5, Tables 3.4 and 3.5). Nickel and Co concentrations in the stream at LU also increased during the onset of drought (Figure 3.4, Table 3.4). A large portion of the Fe was exported from LU during the drought onset event (44.5 %), resulting in higher output of Fe relative to inputs during the study period. Despite elevated concentrations, the low-flow conditions resulted in to exports of only 14.4 % and 15.9 % the total Al and Cu from LU (Table 3.3). In contrast to LU, no large increases in metal concentrations were observed during the onset of drought at the D4 wetland, but there was some evidence of short periods of elevated DIC, DOC, NH_4-N, and NO_3-N (Figures 3.4 and 3.5, Table 3.4).

Discussion

Summer drought resulted in large water table declines and changes in the chemistry of streams draining metal-contaminated wetlands in the Sudbury area. Despite substantial differences in the organic matter content of the peat at D4 and LU, streams at both sites responded similarly to fall re-wetting (following the rise of water tables) although changes in stream chemistry during the onset of drought were quite different between the two sites. Both sites experienced a drought period that lasted over 3 months with streams ceasing to flow for upwards of 10 weeks. In other parts of Ontario it has been shown that drought events lasting even just a few weeks can result in the net export of SO_4 from peatlands (Eimers et al., 2007). During the rewetting period in the fall

there was a large increase in SO_4 concentration and an associated decline in pH in the streams at both sites. Peak SO_4 concentrations in stream water at LU were greater than previously reported values in central Ontario (41.9 mg/L in 1987, Eimers et al., 2007) and parts of the UK (~96.0 mg/L in 1995, Tipping et al., 2003). Both sites experienced a loss of SO_4 relative to inputs, but the difference in magnitude of the SO_4 response between D4 and LU is probably a result of differences in S pool sizes in peat. Both the S pool size and the mean concentrations of SO_4 released during the rewetting period at D4 are approximately 1/3 of that at LU, and deposition of SO_4 to LU is also higher. Even though base cation concentrations increased at both sites during the fall re-wetting events, the pH of both streams fell by about one pH unit as the increase in base cation concentration was unable to compensate for the increase in acid anions. Drought-associated acidification events such as this one have been widely reported in Ontario and other parts of the world (; Clark et al., 2005; Tipping et al., 2003; Lucassen et al., 2002; Dillon et al., 1997; Yan et al., 1996).

There was also an increase in metals at both sites during the rewetting period following drought. The metals that were most responsive to the acidification events (Co, Mn, Ni, and Zn) are all highly mobile at low pH, and Ni in particular does not form precipitates so retention is moderated by adsorption (McLean and Bledsoe, 1992). Post-drought release of metals from peatlands has been documented previously (e.g.: Landre et al., 2009; Adkinson et al., 2008; Tipping et al., 2003) but not to the magnitude demonstrated at these sites. Adkinson et al. (2008) reported that concentrations of Ni and Co in a stream draining a wetland in central Ontario (Plastic Lake) reached values around 3 µg/L, which is several orders of magnitude lower than the observed values at our two sites. Although both sites responded similarly during the fall re-wetting event, increases in metal concentrations as well as base cations and SO_4 were generally

lower at D4 compared with LU despite higher inputs of metals and larger metal pool sizes at D4. It is possible that input estimates are skewed by wind-blown soils within the D4 catchment (which suffered more severe historical disturbance), but metal pool sizes within the wetland are higher regardless. It appears that the magnitude of metal response is closely aligned with the magnitude of SO_4 response (and therefore the size of the S pool within the wetland) and possible organic matter content of the peat, however the potential effect of catchment and hydrology differences cannot be discounted. The D4 wetland lies at the bottom of a much larger catchment than LU, and comprises a much smaller proportion of the total catchment area. It is quite possible that the stream water response to drought is diminished by diluted upland flow with less influence of wetland pore water. Regardless, drought-related metal response was a large portion of the total export at both sites, and responded to SO_4 despite differences in inputs, metal pool sizes, and hydrology.

In the early part of the summer DOC and Fe concentrations LU were much higher than D4, reflecting the fact that the stream drains a more organic-rich wetland. However, during the rewetting period in the fall there was a clear decline in DOC and Fe at LU to values that were similar to those at D4, which changed little during the study period. A post-drought decrease in DOC was also observed by Eimers et al. (2007), and in our case could be a response to the pH decline and a reduction in the solubility of DOC (Evans et al., 2006). However an increase in NO_3-N suggests that the decline in DOC may have been the result of a period of increased decomposition, when nitrification peaked and mineralization of DOC to CO_2 occurred. The decrease in Fe at LU may due to oxidation to insoluble Fe hydroxides and subsequent precipitation under conditions of low pH (Reddy and DeLaune, 2008), however acid conditions were present even prior to the drought and solubility of Fe would always be high, and low Fe

concentrations may instead be simpy a product of less DOC export as much of the Fe is probably in organic forms.

While the stream response to the fall rewetting period was similar, the two wetlands differed in their response to the onset of drought in the early summer. In late June and early July LU experienced a marked increase in concentrations of NH_4-N and DIC followed by NO_3-N. The increase in NH_4-N and DIC suggests enhanced mineralization of organic matter (and increased ammonification) likely in response to elevated temperatures and decreased saturation of peat soils. As the peat continued to dry, oxic conditions led to increased nitrification and the subsequent release of NO_3-N in the stream (Reddy and DeLaune, 2008). There was a much smaller increase in NH_4-N and NO_3-N at D4 during the early part of the summer, which most probably reflects the much lower organic matter content as DOC concentrations were only around 5 mg/L compared with 20 mg/L at LU. It is also possible that the lower amounts of NH_4-N and NO_3-N produced at D4 may be consumed by biological uptake (Reddy and DeLaune, 2008; Williams et al., 1999). A similar response was noted by Watmough et al. (2004) who found that in experimental studies, the increase in NO_3-N concentration in peat with high carbon content was much greater than occurred in organic forest floors with lower carbon content.

There was a release of metals and other covalently bound cations during the onset of drought at LU. During the early part of the summer DOC concentrations in the stream at LU were quite variable but tended to increase from around 15 mg/L at the beginning of June to almost 30 mg/L by late July. The metals that increased (Cu, Fe, and Al) all have a high affinity to bind with DOC (Gensemer and Playle, 1999; McLean and Bledsoe, 1992). In the case of Cu and Fe redox conditions may also be important as stagnant conditions in the wetland and high biological activity may promote reducing conditions that will mobilize these metals (LaZerte, 1991). Nickel

and Co bind to DOC but with less affinity (Reddy and DeLaune, 2008) and were also mobilized during this period, but to a lesser extent than Cu, Fe or Al. Unlike LU, D4 did not experience a pronounced change in metal concentrations during the onset of drought. This may be related to the fact that the water table at D4 took longer to drop below the surface, and so less aeration and oxidation was occurring during this period despite an ammonification event that was of smaller magnitude than at LU. In addition DOC concentration at D4 was low, varying between about 2 mg/L and 6 mg/L and tended to increase during the early part of the summer. This suggests that organic matter is being mineralized at D4 during this period but this has less impact on metals, possibly because pH tended to increase during the same period.

The short-term mobilization of high concentrations of metals following drought has the potential to adversely affect aquatic organisms. A high diversity and abundance of aquatic organisms live in the littoral zones of lakes near steam outflows (Schindler and Scheuerell, 2002; Schindler et al., 1996), and it has also been noted that areas below these streams serve as hotspots of recolonization and diversity because of organic matter inputs (Wesolek et al., 2010; Szkokan-Emilson et al., 2011). The observed metal spikes during the onset of drought would pose a risk to these organisms as well, but the rewetting event would have a greater impact because of elevated concentrations coinciding with high flows. Also, DOC likely played a larger role in the mobility metals during the onset of drought, and these metals would have been in DOC complexes that are potentially less available to biological uptake (Doig and Liber, 2006; McGeer et al., 2002; Marr et al., 1999). Determining the specific toxicity of these mobilized metals is complex, and several speciation models such as Minteq (Allison et al., 1990) and the humic-incorporated WHAM model (Tipping, 1994) have been developed to predict metal speciation and potential availability. Exposed animals also differ in their uptake of available metals, and models have

been developed to predict this uptake, such as the biotic ligand model (BLM) for uptake of Cu and other metals (Di Toro et al., 2000). Regardless of the uncertainty in toxicity, the mobilization of soluble metal species into aquatic systems greatly increases the potential risk. This effect is enhanced by the conditions created following drought in the fall, and this is a time when many larval stages of benthic macroinvertebrates are present in littoral zones of boreal lakes (Huryn and Wallace, 2008).

Conclusion

Drought can have dramatic effects on surface water quality that are short lived, but these episodic events can reach concentrations that are potentially harmful to aquatic life. While there was considerable difference in stream water response during the onset of drought in boreal wetlands that vary considerably in their organic matter content, changes in stream chemistry during the rewetting event were quite similar suggesting the potential for a majority of wetlands in the region to experience this response. These results are important considerations for water quality of boreal surface waters in general, but this study also has particularly important implications for restoration efforts in smelter-impacted areas like Sudbury. Efforts to restore aquatic ecosystems in such areas and protect freshwater resources elsewhere must take into account biogeochemical processes within the entire watershed, especially within wetlands. In addition, disruptions to biogeochemical cycles are likely to become more prevalent and spatial and temporal variation in water chemistry is likely to increase in a time of changing climate.

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Chapter 4. Drought-induced changes in DOM composition and concentration in wetland-draining streams: Implications for metal toxicity in receiving waters

Abstract

Wetlands are a primary source of dissolved organic matter (DOM) to lakes and rivers, and are efficient at storing metals, but they can become sources of many of these metals following water table declines in response to summer droughts. It is expected that these drought-related metal releases are coupled with changes in DOM composition and concentration that could impact potential metal toxicity in receiving waters. Changes in stream chemistry and DOM composition were evaluated at six wetland-draining streams in a heavily metal-contaminated region around Sudbury, Ontario, Canada that experienced drought-related metal releases in the fall of 2011. Differences in DOM concentration (measured as DOC) and composition (determined by PARAFAC and SAC_{340}) between streams were investigated over two years, and drought-related changes were investigated from the spring to fall of 2011. The biotic ligand model (BLM) was used to predict drought-related changes in Ni and Cu toxicity, and the model was ran under a variety of scenarios to estimate the influence of changes in DOM concentration and composition on predicted toxicity. DOM varied in composition and concentration among these six streams, with concentration ranging almost four-fold and SAC_{340} almost three-fold. Sites with high DOM concentrations tended to have more aromatic DOM as well, and experienced the largest drought-related changes in composition and concentration. SAC_{340}

declined by as much as 55 % coupled with a 67 % decrease in DOC concentration. The BLM indicated that increases in Ni concentration played a major role in the increase in predicted toxicity following drought, but that DOM also played a role and concentration was clearly a more significant factor in potential toxicity effects than was the composition of the DOM. The drought-related changes in DOM had a much larger effect on Cu toxicity than on Ni, and predicted Cu toxicity increased following drought primarily because of drought-related DOM changes. Where DOM exhibited large changes, as much as 74 % of the change in predicted Cu toxicity could be attributed to a decline in DOM concentration with an additional 15 % to decreased aromaticity. These processes appear to have regional significance, and the potential for drought-related changes to DOM in concordance with metal release has important implications for wetlands in the boreal regions affected by mining.

Introduction

Wetlands are a primary source of dissolved organic matter (DOM) to lakes and rivers (Mullholland, 2003; Xenopoulos et al., 2003; Gergel et al., 1999; Dillon and Molot, 1997) which influences aquatic ecosystems by regulating light availability and temperature (Snucins and Gunn, 2000; Fee et al., 1996), absorbing UV-B radiation (Molot et al., 2004), and regulating metal availability and water quality (Doig and Liber, 2006; Watras et al., 1998). DOM is commonly measured as dissolved organic carbon (DOC), but it is a heterogeneous mixture of organic molecules with differing aromaticity, molecular weight, and functional groups. For example allochthonous DOM, derived from terrestrial plant material outside of the lake, is more aromatic and has a higher molecular weight than autochthonous material that originates from biological processes within the lake (McKnight et al., 2001). This high molecular weight allochthonous material tends to have more carboxylic and phenolic functional groups that act as sites of reactivity and metal binding (Richards et al., 2001). Weather-related changes in DOC concentrations and exports from wetlands to lakes has garnered considerable attention (e.g.: Eimers et al., 2008; Laudon et al., 2004), however associated changes in DOM composition and its impact on potential metal toxicity has been less-well investigated.

Wetlands are efficient at storing metals, but they can become sources of some metals following drought. Water table declines result in sulphate-related acidification and releases of metal cations such as Co, Mn, Ni, and Zn, and early summer conditions result in increased DOC concentrations and the mobilization of metals such as Cu, Fe, and Al (Landre et al., 2009; Adkinson et al., 2008; Tipping et al., 2003; Chapter 3). This is of particular concern in mining-impacted areas where metal contamination is prevalent and metal releases can reach high concentrations (Chapter 3). Drought conditions are becoming more prevalent in the boreal

ecozone (Trenberth, 2011), and associated water table declines may also result in rapid changes in DOM composition and concentration. For example, Freeman et al. (2001) suggest that warmer temperatures increase the enzyme activity of phenol oxidase, releasing phenolic DOM from peat soils. These phenols can inhibit hydrolase activity, which leads to further increases in pore water and outflow stream DOM concentrations. Despite this temperature response, phenol oxidase is still highly constrained in anaerobic conditions, and the oxidizing conditions brought on by water table decreases can remove this constraint, resulting in the degradation of organic molecules and a decrease in the aromaticity and concentration of DOM (Freeman et al., 2001; Freeman et al., 1993).

DOM structure can influence the mobility, bioavailability, and toxicity of metals, with phenolic, aromatic molecules better able to bind metals such as Cu and Pb (Al-Reasi et al., 2012; Ryan et al., 2004; De Schamphelaere et al., 2004; Schwart et al., 2004). The chelation of DOM with metals results in complexes that are less available for biological uptake, reducing the concentration of bioavailable free ion metals (Richards et al., 2001). Because of this, measures of DOM aromaticity are often used to adjust toxicity models such as the biotic ligand model (BLM: Geiger, 2014; Al-Reasi et al., 2012; Al-Reasi et al., 2011; Richards et al., 2001). Given that metals can be rapidly mobilized from wetlands in response to drought, the potential for coupled changes in DOM release has important implications for ecosystems recovering from combined effects of metal contamination.

The mining region of Sudbury, Canada is one of the most intensively-studied boreal regions in the world in terms of ecosystem recovery from acid and metal impacts. Historical smelter emissions resulted in elevated deposition of S and metals in the region, including Cu, Ni, Co, Zn, Fe, Pb, Cr, and Cd (Adamo et al., 2002; Hazlett et al., 1984; Hutchinson and Whitby, 1977). The

widespread loss of vegetation and soils makes the region particularly prone to high winds and dry conditions (Tanentzap et al., 2007), and Sudbury experienced abnormally dry conditions and above-normal temperatures through July, August and September of 2011 (Environment Canada, 2013; NOAA, 2013). These summer drought conditions resulted in water table declines that affected S and metal cycles in wetlands in the area, resulting in increased export of DOC and metals such as Cu in the early summer, followed by SO_4-mediated export of several metals during rewetting (Chapter 3). It is expected that these metal releases are coupled with changes in DOM composition and concentration that could affect the potential toxicity of metals that are released in stream water. The objective of this study was to evaluate the role of changes in DOM concentration and composition on the potential toxicity of stream water outflow from wetlands affected by drought-related water table declines. Variability in DOM composition was investigated in six wetland-draining streams in the Sudbury area from samples collected over two years (October 2010 to October 2012). Intensive sampling was focused on two of the sites by collecting water samples every 8 hrs with ISCO^{TM} automated samplers from June 2011 to November 2011 to capture changes associated with a drought event. Three main questions are addressed. (Q1) How does DOM composition and concentration differ among the wetland-draining streams? (Q2) How does DOM composition and concentration change in response to drought? And (Q3) do changes in DOM composition and concentration contribute to increased metal toxicity to aquatic biota as assessed with the biotic ligand model (BLM)?

Methods

Site selection and wetland conditions

A preliminary survey of vegetation and annual water table fluctuation in 29 wetlands was conducted in the region in 2010, and peat samples were collected from a subset of 18 wetlands (primarily poor or transitional fens) revealing a wide range in metal and nutrient content (appendix A1). Six of these wetlands were selected because they represented the range of surface peat conditions observed in the regional survey, with sites at the low-ends and high-ends of metal and nutrient concentrations observed regionally (see Appendix A1). They were also selected because they were in a watershed sub-catchment with an outflow draining directly into a lake with a recovering aquatic community (henceforth termed "wetland-influenced catchments"). They were all within 15 km of the active Copper Cliff smelter, however these wetlands would have also been affected by the Coniston smelter that ceased operation in 1972 (See Chapter 2, Table 2.1). Two of the fens occupied smaller portions of their catchments (1.39 and 1.64 % at D4 and D5 respectively) and had shallow organic soil layers (~ 30 cm) overlaying mineral soils with lower organic matter content. The other four wetlands occupied large portions of their catchments (13.5, 10, 5.15, and 20.8 % at C1, C2, BR, LU respectively) and had deeper organic layers (> 50 cm) (See Chapter 2).

Two of the wetlands were selected, a poor fen and a wet meadow (LU and D4 respectively; Figure 4.1), that were also a part of the drought-induced metal release study (Chapter 3). These sites were monitored at a high frequency from June 2011 to November 2011, including a period of drought-related water table decline. HOBO™ water sensors and temperature loggers were installed at 10 and 30 cm depth in three stations spaced evenly in each wetland from 40 m to a

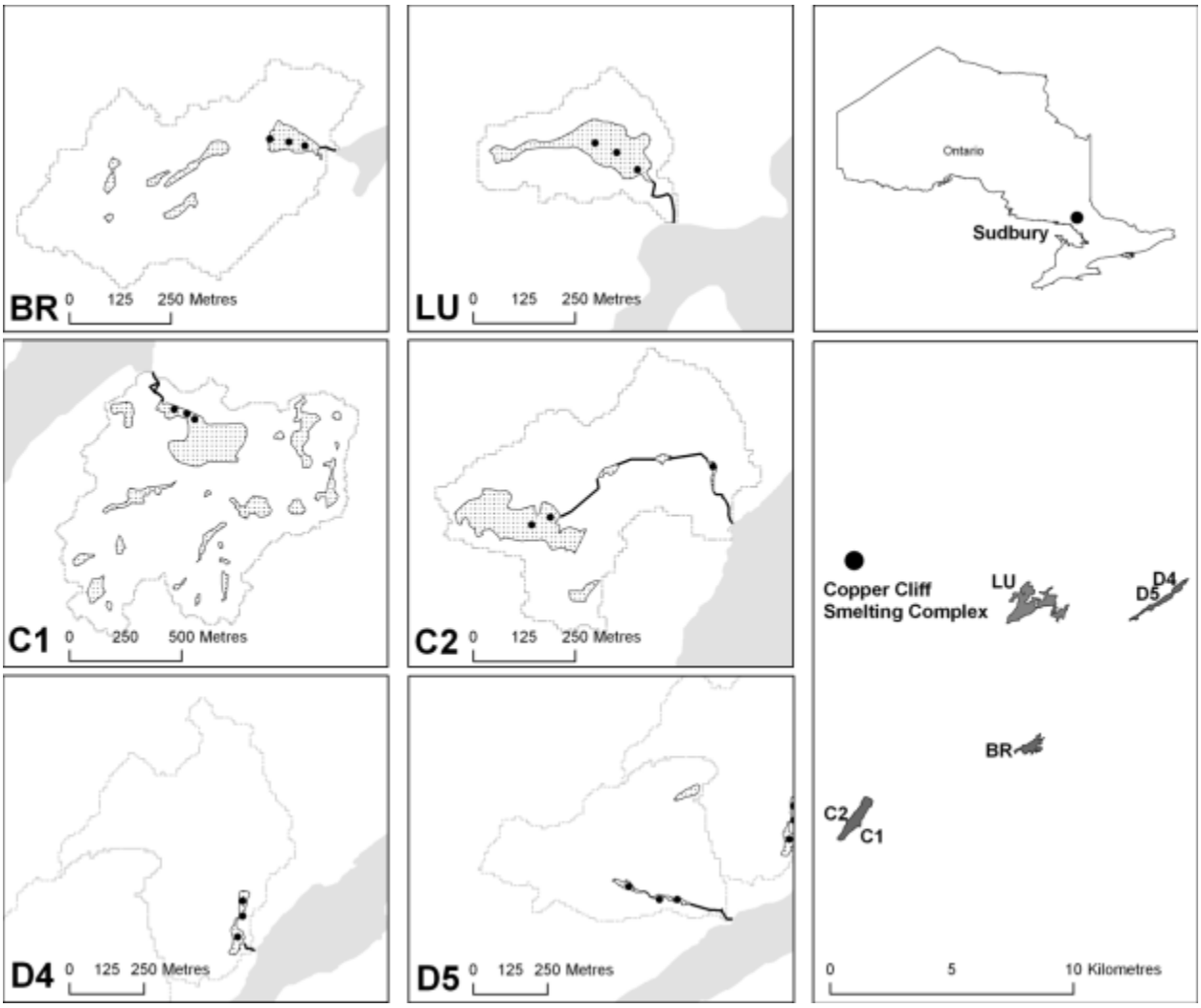

Figure 4.1: Map of six wetlands in their associated catchments in the Sudbury area with streams draining into receiving lakes. Wetland sampling stations are indicated with a solid circle. Sites LU and D4 were part of a drought-related metal release study, and are studied more intensively during the drought conditions in 2011.

maximum of 160 m from the outflow stream, and set to record at 15 minute intervals, from which daily averages were calculated. Stream water levels were recorded at 15 minute intervals with HOBO™ U20 loggers in the outflow streams of LU at D4, and water table height was recorded at 15 minute intervals using TruTrack™ WT-HR 1000 Water Level Loggers installed in a well in the respective wetlands from 0.70 m below ground to 0.30 m above ground. Stream flow was measured across a range of water heights over two years using a Marsh-McBirney Flo-Mate™ 2000 velocity meter. Power rating curves were generated for each catchment, yielding R^2 values of 0.92 and 0.99 for D4 and LU respectively. Discharge for each 15 minute period was estimated from the rating curves and summed to daily totals (Appendix A3).

Water sample collection and analyses

Stream water samples were collected from all six sites every 2 to 4 weeks (depending on rain events and availability of water) from October 2010 to October 2012. Additional samples were collected from the two high-frequency sampling sites (LU, D4) with ISCO™ automated samplers every 8 hours from June 1, 2011 to November 11, 2011 to capture the pre-drought and post-drought responses. Here the pre-drought period is defined as ending on July 27th when stream flow ceases at each site, inclusive of the early drought-onset period discussed in Chapter 3. The post-drought period begins on October 13th when water tables raised to the point that stream flow returned, inclusive of the rewetting period discussed in Chapter 3. Total sample numbers were reduced by periodic low-flow conditions and the drought, for a total of 83 pre-drought samples and 78 post-drought samples at LU. Similarly, 75 post-drought samples were attained from D4, however only 45 pre-drought samples were collected due to intermittent power problems with the ISCO™ automated sampler. Four and six samples were collected during periodic rain-related runoff events through the drought period from LU and D4 respectively.

All water samples were filtered at time of collection with 80 µm Nitex mesh and stream water pH was measured *in-situ* with a Hannah Instruments HI 991003 portable meter and HI 1297 probe. Samples were filtered with 0.2 µm Isopore^{TM} membrane filters and stored at 4 ^{o}C in darkened Nalgene bottles until further analyses. This pore size was chosen to reduce particulates that may increase Tyndall scatter in spectral measurements (Zepp et al., 2004), and to reduce bacterial counts inthe sample. Wang et al. (2007) have shown that 0.2 µm filters increase bacterial removal by an additional 47 % over 0.45 µm filters, providing 97 % or greater removal efficiency.

For biotic ligand modelling, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were analyzed with a Shimadzu TOC-VcpH analyzer, and SO_4 and Cl were analyzed with a DIONEX ICS 1100 ion chromatographer. A portion of the sample was acidified with trace grade HNO_3 and analyzed for total dissolved Ni, Cu, Ca, K, Mg, and Na with a PerkinElmer Optima 7000DV ICP-OES. All containers and equipment were washed in a 10 % HCl acid bath and thoroughly rinsed with TOC-scrubbed Milli-Q A10 water between collections.

DOM concentration was measured as DOC, and composition was determined by measuring aromaticity by sample absorbance and by determining the main DOM fractions with PARAFAC analyses of fluorescence scans, as described below.

Spectral measurements and corrections

Three-dimensional fluorescence scans were performed on the samples with a Cary Eclipse Spectrophotometer at 5 nm excitation steps from 250 to 450 nm, reading emissions at 2 nm steps from 300 to 600 nm (5 nm slit widths). Machines were allowed to warm for 1 hr and samples were scanned at room temperature. The resulting excitation-emission matrices (EEMs) were

instrument corrected and adjusted for inner-filter effects with in-house R scripts (Appendix A5). Inner filter correction was done with sample absorbance measured from 250 to 600 nm using a Varian Cary 60 UV-Vis spectrophotometer according to the methods of Ohno (2002). Rayleigh and Raman scatter areas were cut from the EEMs, and replaced using shape-preserving cubic splice interpolation to remove scatter according to the methods of Bahram et al. (2006) with in-house R scripts (Appendix A5). The blank-subtraction method was not used to remove scatter, as this tends to leave residual scatter and often requires subsequent cutting and interpolating anyways (Zepp et al., 2004).

DOM composition: PARAFAC modelling

A unique parallel factor analysis (PARAFAC) model was generated with 1216 samples from a variety of boreal lake, stream, and wetland sites representing a range of mining-, forestry-, urban-, and fire-related catchment disturbances, but results in this manuscript are restricted to samples from the six aforementioned mining-impacted catchments. The EEMs were normalized by scaling to unit variance, removing covariance between fluorophores and down-weighing the influence of high concentration samples in loadings (Murphy et al., 2013). PARAFAC modelling was done with MATLAB R2013b (Mathworks Inc., Masachusetts, USA) using the N-Way and drEEM toolboxes (Murphy et al., 2013; Andersson and Bro, 2000), with no a priori assumptions of number or shape of components. Model validity was tested with visual analysis of residuals and spectral loadings, and with split-half analysis (Appendix A6). Scores are presented for each sample as F_{max} (maximum intensity) for each component as a percentage of total F_{max} across components. All modelling and analyses were done according to the methods of Murphy et al. (2013) and Stedmon and Bro (2008). Six DOM fractions were identified; two fulvic-like components (C1, C2), two humic-like components (C3, C4), and two protein-like components

(Tyrosine-like C5, Tryptophan-like C6). Protein-like components are summed (C5 + C6) and presented as the total protein-like fraction and fulvic-like components are summed (C1 + C2) and presented as the total fulvic-like fraction, but humic-like components C3 and C4 are kept separate, as they represent low molecular weight (LMW) and high molecular weight (HMW) humic-like fractions respectively (Figure 4.2). Further PARAFAC modelling details and interpretations of components are provided in Appendix A6.

DOM composition: aromaticity

Several absorbance metrics have been developed as estimates of the molecular weight and aromaticity of dissolved organic matter in water samples. These include spectral slopes (Helms et al., 2008), specific UV absorbance at 254 nm (SUVA) (Weishaar et al., 2003) and the specific absorption coefficient (SAC) (Curtis and Schindler, 1997). SAC has been calculated with absorbance measured between 300 and 350 nm, however 340 nm (SAC_{340}) is the wavelength commonly used in metal-mitigation studies and serves as a reliable estimate of metal binding potential (Al-Reasi et al., 2012; Al-Reasi et al., 2011; Schwartz et al., 2004; Richards et al., 2001). Aromaticity was assessed with SAC_{340} as in Curtis and Schindler (1997):

$$SAC_{340} = (2.303 * ABS_{340}) * pathlength\,(cm^{-1}) * 1000\,cm^{3} * DOC_{meas}{}^{-1} \qquad (4.1)$$

Where DOC_{meas} is the measured concentration (mg L^{-1}), and ABS_{340} is absorbance at 340 nm measured on a Varian Cary 60 UV-Vis spectrophotometer in a 1 cm pathlength quartz cuvette. Aromaticity was used as an additional measure of DOM composition, and also to calculate the active DOC concentration (DOC_{actv}) for use in biotic ligand modelling. DOC_{actv} was calculated

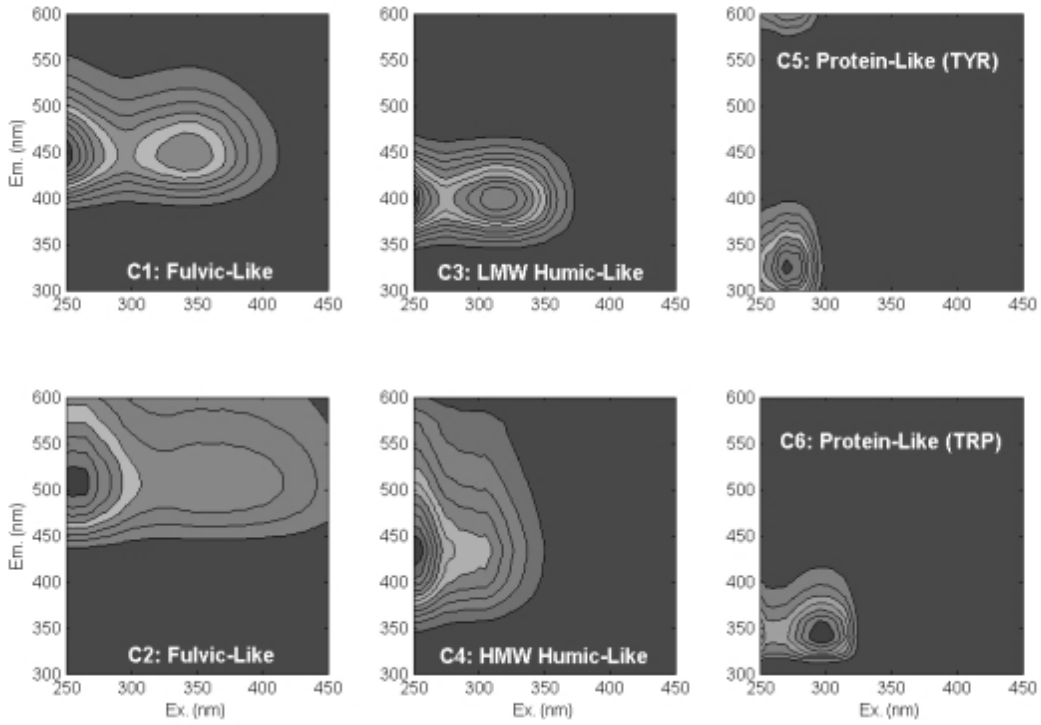

Figure 4.2: Six PARAFAC components representing fractions of DOM. C1 and C2 are fulvic-like fractions and are summed together as total fulvic fraction for analyses. C5 and C6 are tyrosine- (TYR) and tryptophan-like (TRP) fractions, and are summed together as total protein fraction for analyses. C3 and C4 are low molecular weight and high molecular weight humic-like fractions and are kept separate for analyses. See Appendix A6 for details of PARAFAC modelling.

using SAC_{340} and DOC_{meas} as in Schwartz et al., (2004):

$$DOC_{actv} = (0.31 * ln(SAC_{340})) * DOC_{meas} \quad (4.2)$$

DOC_{actv} has been used in place of DOC_{meas} in biotic ligand models (BLMs), offering improved LC50 (concentration for 50 % lethality) and LA50 (metal accumulation that occurs on the biotic ligand at the LC50 resulting in 50 % lethality) estimates for several metals, most notably Cu, Pb, and Ni (Schwartz et al., 2004; Al-Reasi et al., 2011; Al-Reasi et al., 2012; Richards et al., 2001).

Biotic ligand modelling: toxic units

Toxicity of stream water export was predicted both pre- and post-drought using the biotic ligand model (BLM) version 2.2.3 (Paquin et al., 2000). Toxic units were calculated relative to the LA50 (accumulation on the biotic ligand resulting in 50 % mortality) of a ubiquitous aquatic organism (*Daphnia pulex*) such that a value of 1 toxic unit is equivalent to the LA50 metal accumulation for that organism, 2 toxic units is 2 times the LA50 metal accumulation threshold, and so on. The standard BLM critical value of 0.0447 nmol/g_w was used for Cu and the value of 5.1 nmol/g_w derived by Kozlova et al. (2009) was used for Ni (to reach the 48 h LA50 for *D. pulex*), with both values representing the LA50 and 1 toxic unit respectively. Modelling for D4 and LU was done using the average stream water chemistry (pre-drought and post-drought separately) taking DOM composition into account by using DOC_{actv} in place of DOC_{meas}. The effect of stream water toxicity into the lake was determined by calculating toxic units with average stream water and lake water mixed at stream:lake ratios of 1 to 0 at 0.1 ratio intervals, repeated for both pre- and post-drought conditions. For mixing ratios, average Daisy Lake water chemistry was calculated from mid-lake samples collected by the Ontario Ministry of the Environment, with two collected in June and August (pre-drought) and two collected in

September and October 2011 (post-drought). Lake Laurentian water chemistry was not available for 2011 so an average of monthly samples collected by the Nickel District Conservation Authority from May to September 2010 was used. To assess the influence of DOM changes on toxicity, post-drought BLM accumulation calculations were repeated across all dilutions with DOM composition and concentration held constant at pre-drought conditions. The influence of DOM composition was assessed by calculating pre- and post-drought toxic units using DOC_{meas} for comparison with toxic units using DOC_{actv}, thus removing the SAC_{340} adjustment to DOC. BLM models were also generated for the other four sites (C1, C2, BR, and D5) using three spring samples (from May and June 2011) and three fall samples (from October and November 2011) to represent pre- and post-drought periods respectively, for comparison to the high-frequency sampling sites (D4 and LU). BLM data are shown in Appendix A7.

With the exception of PARAFAC analyses and BLM modelling, all analyses and plots were done using R 3.0.3 (R Core Team, 2014).

Results and Discussion

Site differences in DOM composition and concentration

The composition and concentration of DOM varied across the six wetland-draining streams. DOC concentration spanned a three-fold range, with LU having the highest DOC_{meas} and DOC_{actv} and D4 and D5 having the lowest DOC_{meas} and DOC_{actv}. Temporal variability (within-site standard deviations) in DOC_{mean} and DOC_{actv} were highest at sites C1 and LU, and relatively low at all other sites (Table 4.1). The differences in DOC concentration among sites was likely a product of upland influences and peat variability. Sites BR, D4, and D5 had the lowest mean DOC_{meas} (ranging from 3.08 to 7.99 mg/L), and also had the smallest proportion of wetland

within their catchments (10 % or less), with greater upland contributions. The DOC_{meas} values in these wetland-draining streams were comparable with other upland-dominated catchments with peatlands less than 10 % of the total area in streams in southern Ontario where annual DOC concentrations ranged from 2 to 8 mg/L (Eimers et al., 2008). Sites LU and C1 had wetland areas representing 20.8 and 13.5 % of the catchment and mean DOC_{meas} of 11.2 and 9.12 mg/L respectively (Table 4.2, Table 4.3). Variation in peat C content may also have accounted for some of the difference in DOC concentrations between sites, as soils with high C content export more DOC (Aitkenhead and McDowell, 2000) and sites D4 and D5 had peat with lower C content than the other sites, with sites C1 and LU having the highest peat C content (Chapter 2). Pennington (2014) found strong relationships between peat C content and DOC concentration in pore water across 18 surveyed wetlands in the Sudbury area (from which these six sites are a subset).

DOM composition also varied considerably across the six sites, and LU had the most aromatic DOM with SAC_{340} values that were almost three times higher than D4 and over two times higher than D5 (Table 4.1). All six wetland-draining streams had DOM that was dominated by fulvic-like fractions and secondarily by humic-like fractions, with fulvic-like fractions accounting for 50.7 to 59.2 % of the DOM on average. Aromatic DOM with high humic and fulvic-like fractions is characteristic of wetland pore water and wetland-draining streams, and fulvic-like fractions are more labile than humic-like fractions so also tend to increase in stream water below organic soils (Fellman et al., 2010). Sites D4 and D5 had higher protein-like fractions and lowest fulvic-like fractions, and the DOM was the least aromatic at these sites. Protein-like fractions tend to be higher in less organic soils, or sites with less wetland area and higher proportion of upland forest (Fellman et al., 2009). The proportion of low molecular weight

(LMW) and high molecular weight (HMW) humic-like fractions varied between 8.16 and 20.4 % of the DOM across the sites, with the highest LMW and lowest HMW humic-like fractions at the sites D4 and D5. Site LU, which has the highest DOC concentrations and most aromatic DOM, had the lowest LMW and highest HMW humic-like fractions (Table 4.1). LMW humic fractions are characteristic of aquatic systems where high biological activity is occurring, whereas HMW humic fractions are characteristic of highly humified DOM, as in organic-rich peatlands (Fellman et al., 2010).

These differences in DOM composition may also be a result of differences in upland influences especially at D4 and D5, because these sites had the highest upland contribution and lowest wetland area. DOM in the streams draining these catchments could be affected by dilution from upland runoff and a reduction in the relative contribution of wetland-derived compounds, as upland soils tend to export less aromatic DOM (Fellman et al., 2009). There was also considerable difference in the vegetation between the sites, and this too can have an impact on the chemical composition of the leachate and the composition and concentration of peat and DOM (Cuss and Gueguen, 2013; Wickland et al., 2007; Williams et al., 2000; Vitt and Chee, 1990). Site LU was dominated by leatherleaf shrubs (*Chamaedaphne calyculata*) and had a higher peat C content than D4 and D5, which were dominated by grasses and sedges (primarily *Muhlenbergia uniflora*) (Chapter 2).

Drought-related changes to wetland hydrology and peat conditions

In July, August, and September of 2011 LU and D4 experienced lower than normal precipitation (19.6 to 70.6 % of normal) and higher than normal mean temperatures (1.0 to 2.2 ^{o}C higher) (Environment Canada, 2013; NOAA, 2013; see also Chapter 3). Water tables fell below

Table 4.1: Proportions (%) of each PARAFAC-derived fraction in DOM, aromaticity (SAC_{340}), and measured (DOC_{meas}) and active (DOC_{actv}) DOC in mg/L (see text for description) from 6 wetland-draining streams. Averages are from 24 samples collected between October 2010 and October 2012. Sites with an asterix (*) were also monitored at a high frequency, and averages include an additional 167 and 124 samples from collections at LU and D4 respectively between July and November 2011.

	C1	C2	BR	LU *	D4 *	D5
C1 + C2 (Fulvic-like)	56.9 (4.98)	62.0 (4.03)	59.2 (4.59)	58.2 (4.81)	50.7 (7.26)	51.4 (7.83)
C3 (LMW Humic-like)	15.0 (2.64)	16.3 (1.71)	17.7 (3.54)	14.2 (3.44)	20.4 (3.74)	18.4 (4.15)
C4 (HMW Humic-like)	16.0 (4.50)	11.8 (4.96)	10.8 (4.45)	16.9 (5.12)	8.16 (3.04)	11.5 (3.53)
C5 + C6 (Protein-like)	12.1 (6.20)	9.82 (5.61)	12.3 (4.77)	10.7 (6.44)	20.8 (9.66)	16.3 (5.39)
SAC_{340}	24.9 (7.56)	23.4 (5.43)	21.6 (4.77)	32.0 (13.9)	11.9 (4.28)	15.3 (4.55)
DOC_{meas} (mg/L)	9.12 (7.86)	7.99 (1.81)	4.11 (1.65)	11.2 (6.79)	3.08 (0.64)	3.18 (1.14)
DOC_{actv} (mg/L)	7.79 (4.98)	7.81 (1.96)	4.19 (1.61)	12.6 (8.65)	2.28 (0.61)	2.78 (1.04)

the soil surface by July 8th at LU and July 17th at D4. Stream flow ceased at both sites by July 27th (end of the pre-drought period) with intermittent runoff associated with brief rainfall events during the drought at D4, and the monthly mean water table heights fell to 27.5 and 24.9 cm below surface at LU and D4 respectively in August (Figure 4.3). Soil temperatures in the upper 30 cm of the peat reached maximums of 21.8 and 19.2 ^{o}C at LU and D4 respectively in late July, and peat water content in the upper 30 cm fell from pre-drought averages of 53.3 % at both sites to lows of 37.0 and 40.1 % at LU and D4 respectively by mid-September (Figure 4.4). Water tables increased to above-surface levels in late September, followed by the resumption of flow at both sites by October 13th (beginning of the post-drought period) (Figure 4.3). Similar drought-related decreases in water table height and stream flow were also observed at the other four sites (C1, C2, BR, and D5) (see Chapter 2; Figure 2.5).

Drought-related DOM changes

The DOM in the six wetland-draining streams varied in response to drought, but the sites that had high DOM concentrations and highly aromatic DOM exhibited the largest changes in composition and concentration (Table 4.2, Table 4.3). The sites with the highest pre-drought DOC_{meas} (C1 and LU) experienced the largest declines in DOC_{meas} (57.7 % at and 67.4 % declines at C1 and LU respectively) between sites may be due to the low frequency sampling regime at sites C1, C2, BR, and D5. Juckers and Watmough (2014) noted a decrease in DOC concentration in response to laboratory simulated drought in peat samples taken from sites LU, BR and D4, and in-field stream samples are likely to show more variability related in some degree to precipitation and upland inputs. Sites with the highest spring DOC (LU and C1)

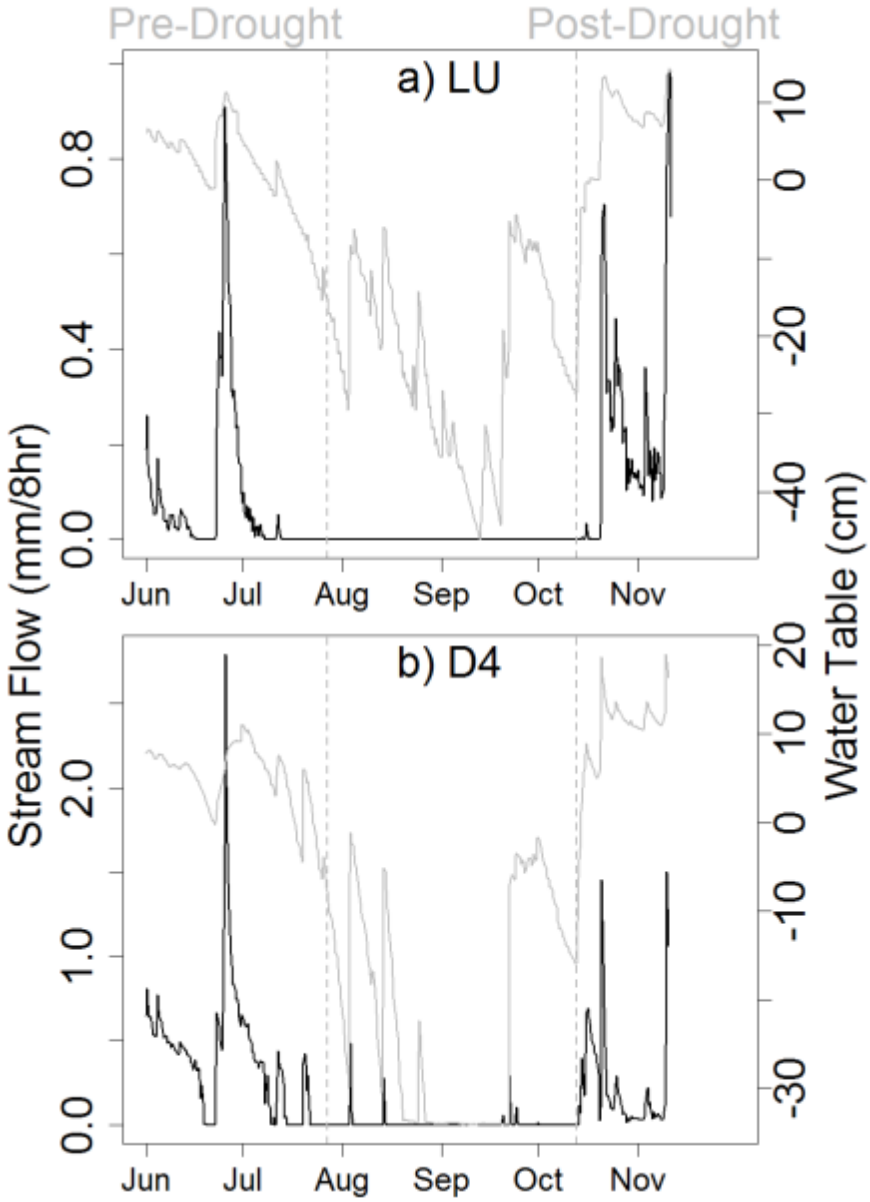

Figure 4.3: Stream flow and water table position at a) LU and b) D4 from June 2011 to November 2011. Pre- and post-drought periods are delineated with dashed vertical lines.

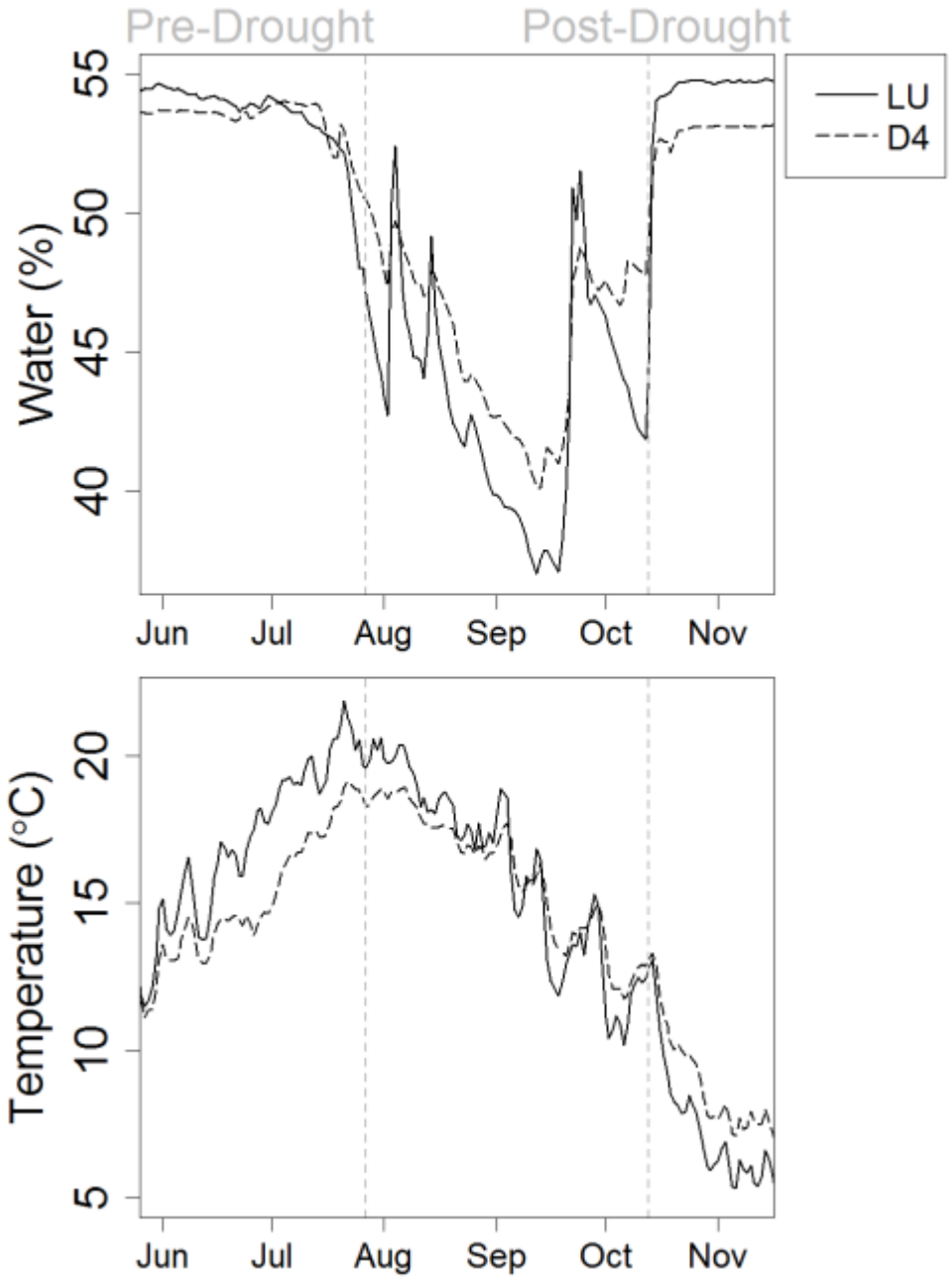

Figure 4.4: Daily soil water content and temperature taken from three probes set at 10 cm and three at 30 cm in LU and D4. Daily values are averages from readings taken every 15 minutes, from June 2011 to November 2011. Pre- and post-drought periods are delineated with dashed vertical lines.

exhibited significant declines in aromaticity (SAC_{340}) with no significant change at the other sites (C2, BR, D4, D5). The combination of decreased DOC_{meas} and SAC_{340} resulted in the significant decrease in DOC_{actv} at C1 and LU as well. There was a large decrease in the HMW humic-like fraction at LU, accompanied by a decrease in the fulvic-like fraction and an increase in the LMW humic-like and protein-like fractions (Table 4.2). In contrast, the largest drought-related change at D4 was an increase in the fulvic-like fraction and decrease in the protein-like fraction. The response of DOM fractions to drought was variable in sites C1, C2, BR, and D5, again likely because of variability in stream water related to precipitation and upland inputs and the low frequency sampling at these sites (Table 4.3).

There have not been any studies of changes in DOM composition in response to drought in boreal wetland systems, but similar changes in DOM aromaticity to those that occurred at C1 and LU have been observed in laboratory studies of pore water DOM in humic peats from the U.K. (Clark et al., 2011) and drought-related increases in the protein-like fraction of DOM have been observed in large subtropical rivers as well (Hong et al., 2011). Wong and Williams (2010) also noted an increase in the protein-like fraction of stream water DOM in fall samples from southern Ontario, as seen in sites C1 and LU where changes in DOM aromaticity occurred. Several studies have also found a reduction in wetland pore water and stream water DOC concentration in response to drought, and there is considerable debate over the mechanism of this change (reviewed by Clark et al., 2010).

It has also been suggested that interactions between metals such as Cu and Fe and DOM can cause quenching (a reduction in intensity) of fluorescence and thus influence spectral measures of DOM, and several metals reached high concentrations in response to the drought (Chapter 3). However, given the low pH of our samples (~ 4 to 5) and the high concentrations of chelating

Table 4.2: Drought-related changes in DOM composition and concentrations of DOC_{actv}, DOC_{meas}, base cations and metals at D4 and LU. Means (standard deviations) are calculated from 83 pre-drought samples and 78 post-drought samples at LU, and 45 and 75 pre- and post-drought samples at D4.

	LU			D4		
	Pre-	Post-	Change (%)	Pre-	Post-	Change (%)
DOM						
Fulvic-like	61.4 (1.26)	55.6 (4.36)	**-9.45**	45.9 (5.05)	54.0 (4.06)	**+17.6**
LMW Humic-like	11.0 (1.18)	17.1 (2.12)	**+55.5**	17.0 (2.10)	22.6 (2.58)	**+32.9**
HMW Humic-like	21.3 (2.58)	13.1 (3.31)	**-38.5**	10.3 (1.79)	6.53 (2.19)	**-36.6**
Protein-like	6.27 (1.63)	14.1 (5.61)	**+125**	26.8 (7.79)	16.9 (4.38)	**-36.9**
SAC_{340}	45.5 (7.44)	20.1 (3.12)	**-55.8**	13.6 (2.32)	10.8 (3.68)	**-20.6**
DOC_{meas} (mg/L)	17.9 (4.29)	5.83 (0.46)	**-67.4**	3.21 (0.75)	3.06 (0.54)	**NS**
DOC_{actv} (mg/L)	21.1 (5.07)	5.40 (0.50)	**-74.4**	2.57 (0.62)	2.17 (0.49)	**-15.6**
Metals and Sulphate						
Cu (µg/L)	137 (114)	61.2 (25.6)	**-55.3**	31.1 (16.7)	36.7 (14.4)	**NS**
Ni (µg/L)	166 (118)	713 (398)	**+330**	61.3 (26.8)	217 (108)	**+254**
SO_4 (mg/L)	1.73 (1.45)	52.1 (30.8)	**2911.6**	5.11 (1.86)	17.2 (9.37)	**236.6**
pH and base cations						
pH	5.00 (0.21)	4.14 (0.21)	**-17.2**	4.77 (0.23)	4.08 (0.24)	**-14.5**
Ca (mg/L)	1.53 (0.71)	13.8 (7.08)	**+802**	0.76 (0.44)	2.87 (1.31)	**+278**
Mg (mg/L)	0.31 (0.14)	2.55 (1.32)	**+723**	0.31 (0.16)	1.13 (0.54)	**+265**
Na (mg/L)	0.59 (0.32)	1.51 (0.30)	**+156**	0.87 (0.36)	1.39 (0.37)	**+59.8**
Toxicity						
Cu (T.U.)	27.0	172	**+537**	118	150	**+27.1**
Ni (T.U.)	0.04	0.60	**+1400**	0.18	0.53	**+194**

* All changes were significant ($p < 0.01$) based on student's T-Tests, unless indicated with NS.

Table 4.3: Changes in DOM composition and concentrations of DOC_{actv}, DOC_{meas}, base cations and metals from spring to fall of 2011 at C1, C2, BR, and D5. Means (standard deviations) are calculated from three spring and three fall samples.

	C1			C2			BR			D5		
	Spring	Fall	Change (%)	Spring	Fall	Change (%)	Spring	Fall	Change (%)	Spring	Fall	Change (%)
DOM												
Fulvic-like	57.2 (1.11)	51.3 (6.31)	**NS**	59.8 (7.45)	61.7 (3.89)	**NS**	57.9 (1.50)	61.5 (2.00)	**NS**	38.6 (6.50)	48.7 (3.86)	**NS**
LMW Humic-like	14.1 (1.70)	16.9 (1.56)	**19.9**	17.5 (1.30)	16.8 (0.85)	**NS**	17.7 (3.18)	17.3 (0.98)	**NS**	10.9 (6.20)	20.2 (1.54)	**NS**
HMW Humic-like	12.9 (3.04)	14.6 (1.07)	**NS**	5.76 (3.98)	11.9 (2.38)	**107**	8.49 (2.61)	11.8 (1.69)	**NS**	6.50 (0.71)	11.8 (1.61)	**NS**
Protein-like	15.8 (2.87)	17.2 (6.20)	**NS**	17.0 (9.91)	9.54 (2.90)	**NS**	15.9 (2.02)	9.52 (1.29)	**-40.1 ***	24.0 (0.42)	19.4 (3.01)	**NS**
SAC_{340}	37.8 (18.4)	18.4 (8.06)	**-51.3**	18.5 (9.89)	22.9 (1.84)	**NS**	23.2 (3.07)	15.7 (2.51)	**NS**	16.0 (0.28)	15.6 (1.02)	**NS**
DOC_{meas} (mg/L)	10.4 (3.80)	4.40 (0.64)	**-57.7**	8.06 (1.82)	8.80 (1.40)	**NS**	2.26 (0.80)	4.49 (0.24)	**98.7 ***	3.39 (1.05)	2.37 (0.13)	**NS**
DOC_{actv} (mg/L)	11.6 (4.05)	3.95 (1.19)	**-65.9**	7.15 (3.05)	8.55 (1.56)	**NS**	2.67 (0.41)	3.98 (0.07)	**NS**	3.03 (1.27)	2.02 (0.13)	**NS**
Metals and Sulphate												
Cu (µg/L)	40.8 (6.68)	17.4 (7.30)	**-57.4 ***	19.0 (4.75)	22.6 (2.77)	**NS**	15.4 (3.35)	16.1 (4.49)	**NS**	16.1	7.33 (0.18)	**NS**
Ni (µg/L)	59.7 (48.8)	210 (51.6)	**252 ***	69.6 (36.4)	89.5 (48.1)	**NS**	56.6 (15.9)	149 (42.1)	**163 ***	64.7 (40.5)	166 (57.2)	**157**
SO_4 (mg/L)	2.39 (2.08)	26.8 (5.81)	**1021 ***	5.72 (0.43)	16.9 (1.93)	**195 ***	6.75 (6.18)	12.6 (1.82)	**NS**	8.05 (1.50)	19.3 (3.48)	**140 ***
pH and base cations												
pH	5.28 (0.20)	4.26 (0.90)	**NS**	5.14 (0.26)	4.84 (0.04)	**NS**	4.73 (0.31)	4.34 (0.03)	**NS**	5.57 (0.30)	4.93 (0.52)	**NS**
Ca (mg/L)	1.56 (0.23)	5.96 (1.15)	**282 ***	10.4 (7.18)	13.7 (1.56)	**NS**	1.04 (0.23)	3.03 (0.39)	**191 ***	1.34 (1.23)	4.82 (1.07)	**260 ***
Mg (mg/L)	0.54 (0.04)	2.09 (0.32)	**287 ***	1.52 (1.05)	1.98 (0.28)	**NS**	0.43 (0.13)	0.97 (0.10)	**126 ***	0.46 (0.32)	2.18 (0.72)	**374 ***
Na (mg/L)	1.45 (0.13)	2.09 (0.90)	**NS**	10.4 (6.03)	8.89 (0.87)	**NS**	0.74 (0.18)	1.24 (0.21)	**67.6 ***	1.10 (0.42)	1.93 (0.52)	**75.5**
Toxicity												
Cu (T.U.)	24.9	65.6	**163**	38.7	56.5	**46**	59.3	53.3	**-10**	26.5	59.9	**126**
Ni (T.U.)	0.04	0.32	**700**	0.06	0.07	**14**	0.16	0.32	**100**	0.19	0.29	**57**

* All changes were significant ($p < 0.10$) based on student's T-Tests, unless indicated with NS. Significance with $p < 0.05$ is indicates with an asterix (*).

metals both before and after drought (in some cases higher prior to drought, particularly the chelating metals Cu and Fe) (Table 4.2), it is unlikely that quenching is playing a major role in the observed DOM changes (see Appendix A6 for further discussion).

Potential mechanisms of drought-related DOM changes

Microbial mechanisms have been proposed for the decline in DOC concentration following drought, either through enhanced respiration (i.e.: decomposition) or decreased production of DOC (Clark et al., 2005; Fenner et al., 2005; Pastor et al., 2003; Scott et al., 1998). Others have proposed that DOC solubility is decreased with increased acidity and ionic strength brought on by sulphur oxidation (Clark et al. 2011; 2006; 2005). In this study, a comparable post-drought spike in sulphate (SO_4) and a decrease in pH is seen at all sites (Table 4.2, Table 4.3), but large DOC declines only occur at LU and C1 where the largest aromaticity decreases occur (Table 4.2, Table 4.3), suggesting that solubility is not the dominant mechanism of DOC decline.

Focusing on the more intensively monitored sites with higher frequency samples (LU and D4), the DOC decline appears to be related to the changes in DOM composition, with a strong positive correlation between DOC_{meas} and SAC_{340} that holds across sites. This increase in SAC_{340} was also related to the shift from HMW to LMW humic fractions, and was correlated less-strongly with the fulvic-like DOM fraction and negatively to the protein-like DOM fraction (Table 4.4). This relationship between changes in molecular weight and absorbance is consistent with other studies. Cuss and Gueguen (2013) found a positive correlation between optically-derived measures of composition and aromaticity and measures of molecular weight in plant leachate DOM samples, and also noted that samples with higher protein-like fractions were of lower molecular weight. There was a large post-drought increase in the protein-like fraction at

Table 4.4: Pearson correlation coefficients between DOC concentration (DOC_{meas}) and measures of DOM composition in 124 and 167 samples collected from D4 and LU respectively between June 2011 and November 2011 including a period of drought.

	DOC_{meas}	$log(SAC_{340})$	LMW Humic	HMW Humic	Protein	Fulvic
DOC_{meas}	-					
$log(SAC_{340})$	0.814	-				
LMW Humic	-0.794	-0.832	-			
HMW Humic	0.859	0.853	-0.912	-		
Protein	-0.653	-0.555	0.339	-0.622	-	
Fulvic	0.615	0.518	-0.298	0.522	-0.971	-

LU where these molecular weight changes occurred, which is indicative of a higher fraction of microbially-derived DOM (Table 4.2). The anaerobic conditions of wetlands usually restrict phenol oxidase activity, reducing the breakdown of phenolic compounds further suppressing decomposition of organic molecules by inhibiting hydrolase activity (Freeman et al., 2004; Williams et al., 2000) and by binding to and reducing the bioavailability of more labile organic molecules (Scully et al., 2004). Following this reasoning the aromatic, phenolic DOM at LU could have suppressed decomposition of organic molecules and led to elevated DOC_{meas} during anaerobic conditions that occurred in the spring, while the oxidizing conditions occurring during the drought would then remove this inhibition and result in rapid respiration and a decline in DOC_{meas} (Freeman et al., 2004) (Table 4.2).

Phenolic, aromatic molecules are also more susceptible to photo-degradation (Kellerman et al., 2014; Kelton et al., 2007; Kujawinski et al., 2004), which can also cause a decrease in DOM concentration and a shift from HMW to LMW DOM (Porcal et al., 2014; Bertilsson and Tranvik, 2000). Porcal et al. (2014) found photo-degradation to result in a decrease in absorbance (integrated from 250 to 450 nm) and concentration by as much as 99 and 49 % respectively. The

rate of photo-degradation is further accelerated at lower pH through the oxidation of DOC by hydroxyl radicals (Porcal et al., 2014; Molot et al., 2005; Anesio and Graneli, 2003; Gennings et al., 2001), and the production of oxidizing hydroxyl radicals is enhanced by the presence of iron (Molot et al., 2005; Voelker et al., 1997). A decrease in DOM concentration may also occur with the interaction of Ca and byproducts of degradation to form $CaCO_3$, which in turn can co-precipitate DOM (Porcal et al., 2014; Stewart and Wetzel, 1981). In our study the drought conditions at LU resulted in both elevated base cations (including Ca) and decreased pH, and these combined conditions would favour accelerated photo-degradation.

It is also possible that during the post-drought conditions there is a higher relative contribution of upland versus wetland-derived flow and DOM. Upland soils tend to have lower HMW and higher LMW humic-like fractions of DOM that are less aromatic, as well as higher protein-like fractions (Fellman et al., 2009). Fellman et al. (2009) noted similar increases in protein-like fluorescence in wetland-draining stream samples in both the fall and the spring when flows are high, suggesting that these changes may occur as a result of high flow and dilution with upland-derived inputs .

Drought-related metal release: BLM-predicted toxicity

There was an increase in BLM-predicted toxic units (T.U.) of Ni following drought. The predicted toxicity of Ni in LU stream water was 0.04 T.U. before the drought, and was higher at D4 (0.18 T.U.) despite lower Ni concentrations because of low concentrations of ligand-competing base cations (Table 4.2, Table 4.5). Following the drought, predicted toxicity of Ni increased 1500 % to 0.45 T.U. at LU and 300 % to 0.39 T.U. at D4. Post-drought Ni

Table 4.5: Post-drought and drought-related change in Ni, Cu, and DOC concentrations (DOC_{actv} as used in toxicity calculations), and toxicity of Ni and Cu in toxic units relative to the 48 hr LA50 for D. pulex. *Values are taken from an average of two samples in June (pre-drought) and November (post-drought) of 2011. Values from sites with an asterix (*) (high intensity sampling sites) are calculated from 83 and 45 pre- drought samples and 78 and 75 post-drought samples at LU and D4 respectively.*

	Post-Drought					Change (% of Pre-Drought)				
	Ni (mg/L)	Ni (T.U.)	Cu (mg/L)	Cu (T.U.)	DOC_{actv}	Ni (mg/L)	Ni (T.U.)	Cu (mg/L)	Cu (T.U.)	DOC_{actv}
BR	142	0.33	18.7	58.4	3.93	447	420	113	91.1	133
C1	205	0.43	13.7	50.0	4.54	435	1819	31.1	279	33.9
C2	83.6	0.09	22.1	59.4	7.65	111	141	127	146	105
LU *	713	0.45	61.2	172	5.4	430	1500	44.7	637	25.6
D4 *	217	0.39	36.7	150	2.17	354	300	118	127	84.4
D5	134	0.22	13.7	92.2	1.9	144	124	69.5	128	97.4

concentrations were over 3 times higher at LU than D4 but higher base cation concentrations reduced the predicted toxicity of Ni at LU to levels comparable to D4 (Table 4.2, Table 4.5). The other sites (C1, C2, BR, D5) also experienced similar increases in predicted Ni toxicity from spring to fall, with lower magnitude of change at C2 and D5 where Ni concentrations did not increase as much (Table 4.5).

There was also an increase in BLM-predicted toxic units (T.U.) for Cu following drought. The predicted toxicity of Cu in stream water was 27 and 118 T.U. at LU and D4 respectively before the drought. Pre-drought Cu concentrations were higher at LU than D4 but T.U. was again lower at LU, this time primarily because high DOM concentrations reduced free ion Cu (Table 4.2, Table 4.5). Following the drought, mean Cu concentration decreased at LU and did not significantly change at D4, but drought-related DOM changes affected predicted free-ion concentrations and T.U. at both sites. Predicted toxicity of Cu increased 637 % at LU following drought, to 172 T.U. (Table 4.5), and changed comparatively less at D4 following the drought, but still increased 127 % to 150 T.U. All of the other sites also experienced similar increases in Cu T.U. following drought, with a drop in T.U. only at BR where DOC_{actv} increased in response to drought (Table 4.5). The toxicity of Cu was considerably higher than that of Ni in general because the critical accumulation of Cu required to elicit toxicity (where T.U. equals 1) is much lower for Cu (0.0447 nmol/g_w; BLM value) compared to Ni (5.1 nmol/g_w; from Kozlova et al., 2009).

These drought-related increases in toxicity extend into the lake and have the potential to impact lake communities. Prior to the drought, lake water dilution had little effect on the predicted toxicity of Ni at either LU or D4 and remained below 0.20 T.U. in all cases. Following the drought, stream water from both sites required full dilution with lake water to return the

predicted toxicity to pre-drought conditions (Figure 4.5). Predicted stream water Cu toxicity was considerably higher at both sites, and required full dilution with lake water to reach low levels comparable to that of Ni. There was an increase in predicted Cu toxicity of stream water at both sites as it mixed with lake water after the drought, reaching maximum toxicity at stream-to-lake ratio of 0.9 to 0.8, with the same observed before the drought at LU (Figure 4.5). This is because both hydrogen ions and other cations have a high affinity for biotic ligands and DOC (Di Toro et al., 2001), and there was a more rapid decline in ligand-competing hydrogen ions than in Cu concentrations with lake water dilution, thus decreasing competition and increasing the binding of Cu to the biotic ligand (Appendix A7).

The predicted toxicity of Cu was considerably higher than that of Ni, but although the toxicity of Ni did not reach the LA50 for *D. pulex* at any of the sites (T.U. remained below 1), this does not mean that Ni was not toxic. It should be noted that the *D. pulex* LA50 values used in BLM modelling are for 48 h exposure, and these conditions may remain toxic for several weeks (see Chapter 3). These conditions may also be quite toxic for other organisms. For example, Keithly et al. (2004) found the LA50 for *Ceriodaphnia dubia* to be 1.92 units, almost 75 % lower than the critical accumulation used to calculate T.U. for *D. pulex*. Others have also found lower values required to reach the LA50 for *D. pulex* (see Kozlova et al., 2009), so it is cautioned that T.U. is used only as a relative measure used to illustrate the change in toxicity associated with drought and should be interpreted as such. However, it should be noted that Komjarova and Blust (2008) demonstrated a suppression of Ni uptake by *Daphnia magna* through competitive interaction with Cu, suggesting that the main mechanism of toxicity in these systems could be Cu.

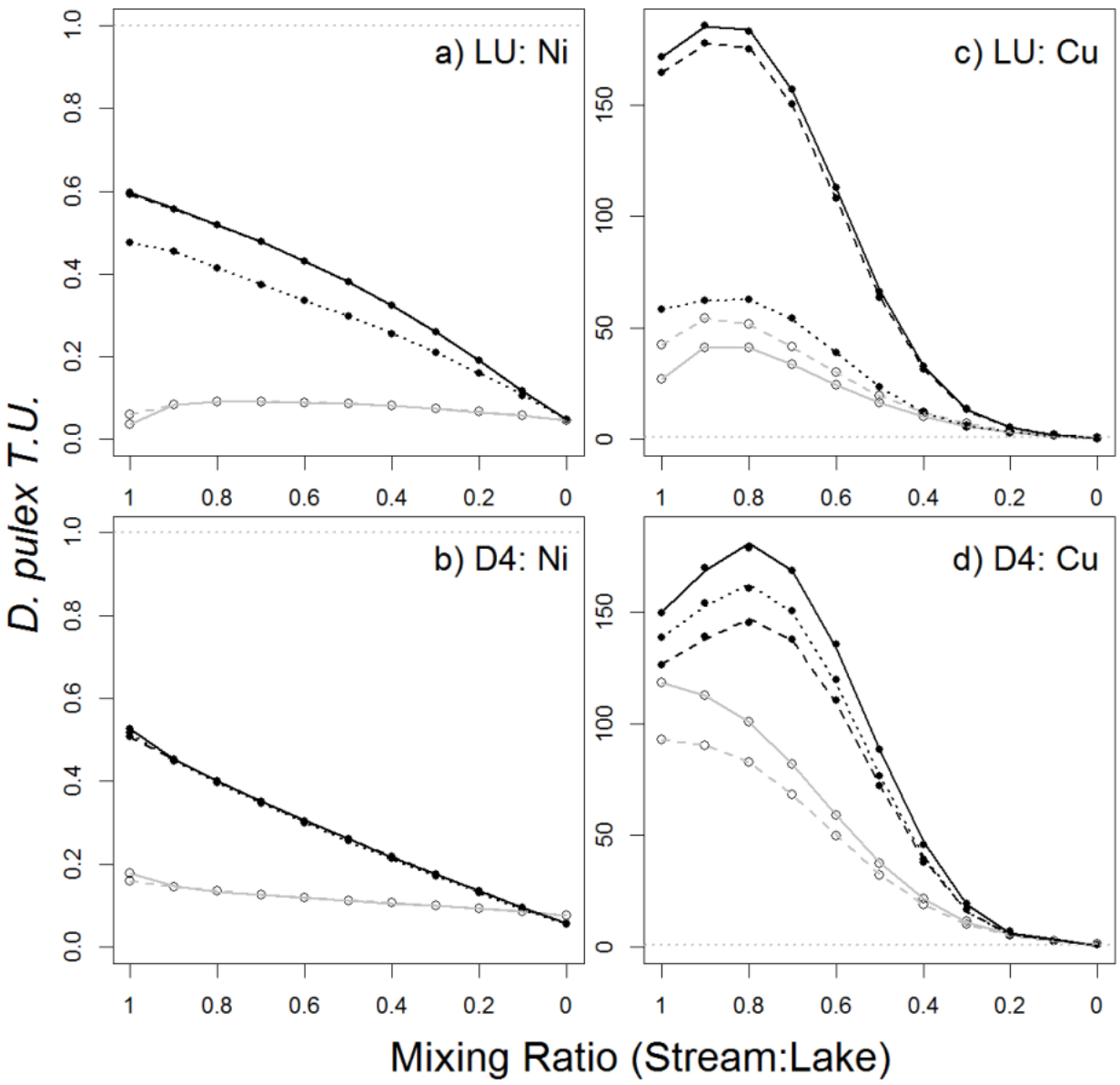

Figure 4.5:Biotic ligand model (BLM) predicted toxicity for Ni in a) LU and b) D4, and Cu in c) LU and d) D4 with stream water mixed with receiving lake water. Toxicity is presented in toxic units (T.U.), scaled such that 1 toxic unit is equal to the LA50 for D. pulex. Solid lines represent the actual toxicity with DOM aromaticity considered (using DOC_{actv}) and dashed lines represent predicted toxicity without aromaticity considered (using DOC_{meas}), for both pre-drought (grey lines) and post-drought (black lines). The dotted black lines represent post-drought toxicity if there were no change in DOC concentration or composition, calculated using the pre-drought DOC_{meas}.

The role of DOM in toxicity changes

The increases in Ni concentration played a major role in the increase in predicted toxicity in response to drought, but DOM also played a role and concentration was clearly a more significant factor in potential toxicity effects than was the composition of the DOM. This can be illustrated by showing that if DOC_{meas} is used instead of DOC_{actv} to calculated Ni toxicity (i.e. disregarding aromaticity changes) the total drought-related change in toxicity is reduced by 5 % at LU, but if both concentration and aromaticity of DOM are held constant (using pre-drought DOC_{actv} both pre- and post-drought) the drought-related change in toxic units dropped by 21 %. This suggests that changes in concentration are responsible for approximately 16 % of the increased toxicity at LU, with aromaticity contributing an additional 5 %. In contrast, neither concentration nor aromaticity had any influence on the change in Ni toxicity at D4, as there were minimal changes in DOM composition and quality at that site (Figure 4.5). These findings are consistent with Kozlova et al. (2009) and Geiger (2014) who both found that DOM was able to mitigate Ni toxicity, and that this mitigative potential differed with varying sources of DOM. Geiger (2014) also found that DOM quality had less overall effect on mitigation than DOC concentration.

The drought-related changes in DOM had a much larger effect on predicted Cu toxicity than it had on Ni. The changes in DOM after the drought resulted in increased Cu toxicity at LU despite decreases in Cu and increases in ligand competing base cation concentrations. The stream water DOM at LU was highly aromatic prior to the drought (DOC_{actv} was higher than DOC_{meas}), but the loss of aromaticity following drought reduced metal-binding capacity (lower DOC_{actv} than DOC_{meas}) and increased free ion Cu. When disregarding aromaticity in toxicity calculations (using DOC_{meas} instead of DOC_{actv} as done for Ni earlier) the total change in Cu toxicity

decreased by 15 %. Holding both concentration and aromaticity constant in calculations (using pre-drought DOC_{actv} both pre- and post-drought) decreased the drought-related toxicity change by 89 %, suggesting that changes in concentration are responsible for approximately 74 % of the increased Cu toxicity at LU with aromaticity contributing an additional 15 % (Figure 4.5). This is consistent with several studies that have found DOM to strongly mitigate the toxicity of Cu (e.g.: Al-Reasi et al., 2012; Kim et al., 1999), as Cu has a higher affinity for DOM than Ni (Carbonaro et al., 2011). While predicted Ni toxicity increased because of drought-related increases in Ni concentrations and decreases in concentrations of ligand-competing base cations, predicted Cu toxicity increased primarily because of drought-related DOM changes.

In contrast to LU, stream water DOM at D4 was less aromatic both pre- and post-drought (as discussed earlier), and DOC_{actv} was always lower than DOC_{meas}. There was no drought-related change in DOC_{meas}, but SAC_{340} and DOC_{actv} decreased (Table 4.2). Without any changes in DOM concentration or aromaticity at D4, the estimated post-drought toxicity dropped by 36 %, and the total change in toxicity remained the same when disregarding aromaticity in calculations (Figure 4.5). This suggests that the small (statistically insignificant) change in DOC concentration accounted for 36 % of the drought-related change in toxicity at D4, and the minor (but significant) drought-related changes in aromaticity were not enough to change toxicity. Despite no drought-related effect of aromaticity, pre- and post-drought toxicity estimates dropped by 22 and 15 % respectively when aromaticity was disregarded in calculations (Figure 4.5). This suggests that the less-aromatic DOM at D4 offered poor metal-mitigating potential at all times regardless of the drought, and coupled with low DOC_{meas} resulted in post-drought toxicity at D4 almost as high as LU despite much lower Cu concentrations (Table 4.5).

Conclusion

DOM composition and concentration differed among sites, and where concentration was higher so was aromaticity and proportion of HMW humic-like fractions (Q1). Where DOM concentration and aromaticity was high, there were large decreases in aromaticity coupled with decreased concentrations following summer drought. Comparatively little change was observed where DOM concentration and aromaticity was low to begin with (Q2). The increases in Ni concentration played a major role in the increase in predicted toxicity in response to drought, but DOM also played a role and concentration was clearly a more significant factor in potential toxicity effects than was the composition of the DOM. The drought-related changes in DOM had a much larger effect on Cu toxicity than it had on Ni, and while predicted Ni toxicity increased because of drought-related increases in Ni concentrations and decreases in concentrations of ligand-competing base cations, predicted Cu toxicity increased primarily because of drought-related DOM changes. Where DOM exhibited large changes, as much as 74 % of the change in predicted toxicity could be attributed to a decline in DOM concentration with an additional 15 % to decreased aromaticity. Predicted toxicity increased at all sites following drought suggesting regional significance, but varied depending on DOM composition and concentration differences which changed following summer drought. This has obvious implications for recovering aquatic communities that are living in the near shore areas of lakes and other receiving waters, particularly as dry conditions and water table declines become more prevalent as climates warm in boreal regions affected by mining.

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Chapter 5. General Conclusion and Mitigation Recommendations

Summary of Findings

The findings of this study have advanced our understanding of the function of boreal wetlands in terms of regulating metal fluxes and associated toxicity in catchments that are recovering from aerial deposition of metals. The wetlands have provided important ecosystem services by adsorbing large concentrations of metals over decades of emissions. However it is now apparent that followingdeclines in deposition of smelter-related metals in the region the wetlands remain heavily contaminated and that the export of metals has decreased comparatively less than atmospheric inputs since the 1970's (Chapter 2). Current exports of metals from these wetlands translates into inputs to lakes that exceed current atmospheric deposition in some cases, and this source of metal contamination to aquatic ecosystems was unrecognized before this study. This has important implications for the recovery of aquatic communities that may be reliant upon wetland-sources of terrestrially derived organic matter, and and provides new insight into the recovery trajectory of aquatic ecosystems in the Sudbury area.

This study has also furthered our understanding of the temporal dynamics of mining-impacted landscapes. There was a release of metals that have a high affinity for dissolved organic matter (DOM) from some wetlands in the summer when flows were low, but drought conditions resulted in the release of SO_4-related metals over relatively short time periods following rewetting and the return of flow and accounted for large fluxes of metals (Chapter 3). Although it has been known for some time that metals can be mobilized from wetlands when water table

declines result in the oxidation of sulphur and the subsequent formation of sulphuric acid, the magnitude of this response exceeded any previously documented drought-related metal releases. Efforts to restore aquatic ecosystems and protect freshwater resources must take into account these potentially toxic metal pulses, as drought-related disruptions to biogeochemical cycles are likely to become more prevalent in a changing climate.

This study has also furthered our understanding of the complex interactions between dissolved organic matter (DOM) and metals in smelter-impacted watersheds, revealing that drought-related DOM changes act to exacerbate metal toxicity to aquatic organisms (Chapter 4). Sites with high DOM concentrations tended to have more aromatic DOM as well, and these sites experienced the largest drought-related declines in both concentration and aromaticity. Biotic ligand modelling predicted that increases in Ni concentration played a major role in increasing predicted toxicity in response to drought, but that changes in DOM was also important. The drought-related changes in DOM had a much larger effect on Cu toxicity than it had on Ni, and predicted Cu toxicity increased primarily because of drought-related DOM changes. Where DOM exhibited large changes, as much as 74 % of the change in predicted Cu toxicity could be attributed to a decline in DOM concentration with an additional 15 % to decreased aromaticity. This is important because it adds a new dimension to the temporal variability in metal release and toxicity, and reveals that metals that were not released by SO_4-related processes can also be experiencing increases in potential toxic effects. This is also one of very few studies to incorporate temporal changes in DOM composition in a natural system into biotic ligand modelling of toxicity.

The findings of this study are important both locally within the Sudbury region and throughout the boreal ecozone where peatlands are dominant and localized mining operations may occur. It

is estimated that 25 % of the world's wetlands are within the boreal ecozone of Canada alone, and many of these wetlands are hydrologically connected to freshwater lakes and rivers in a region that experiencing ongoing and expanding metal mining operations (Wells et al., 2011). Not only are the findings from this study important to areas affected by smelter-related aerial deposition of metals, but it also has important implications to cases where constructed natural wetlands are mitigating mining-related aqueous effluents. Although the source is different, the mechanism of metal binding is the same for both aqueous and aerial sources of metals and much of the aerial input to wetlands can come from aqueous upland runoff. While this thesis did not specifically address the mitigation of aqueous effluents by wetlands, an ongoing study is addressing exactly this (see work by Varun Gupta). This study can also contribute to the advancement of local restoration efforts in the Sudbury region, and so mitigation recommendations are provided. First the question of how long it will take to deplete metal stores in these wetlands is addressed, and then recommended strategies to minimize the release of high concentrations of toxic metals to receiving waters are provided. Suggestions of how to selectively target wetlands for mitigation efforts are also offered.

How Long Will it Take for Peat Metal Stores to Deplete?

Prior to the mining operation in Sudbury, wetlands in the area would have been relatively uncontaminated, with metal concentrations reflecting background levels or perhaps early North American industry. Logging of red and white pine began in the Sudbury region in 1872, and the subsequent development of rail lines led to the discovery of ore deposits. The first roast yard was set up by 1888, and these early roast beds resulted in heavy destruction and contamination of localized areas. By 1929 roast beds were abandoned for smelting, which was more efficient but dispersed pollutants over a greater area (Winterhalder, 1995). These smelter emissions resulted

in elevated deposition of S and metals in the region, including Cu, Ni, Co, Zn, Fe, Pb, Cr, and Cd (Adamo et al., 2002; Hazlett et al., 1984; Hutchinson and Whitby, 1977).

During the early years of smelter-related deposition, wetlands in the Sudbury area were providing a very important ecosystem service, by taking up high concentrations of metals and keeping them out of surface waters. Although there is some debate over the mechanism(s) of the uptake of metals by peat, it is generally accepted to occur primarily through chelation with carboxylic and phenolic functional groups, exchanging for protons and other cations on those sites (Reddy and DeLaune, 2008; Brown et al., 2000). The partitioning of metals between soil pore water and peat is an equilibrium exchange reaction regulated by total metals, and affected primarily by organic matter content (as an exchange medium) and pH (Sauvé et al., 2000). During the early years of smelter-related deposition, equilibrium partitioning between pore water (with high concentrations of deposited metals) and peat (initially with low metal content) would have been in favour of adsorption (Brown et al., 2000). Elevated deposition from local smelters continued to a peak in the 1960s, and a net uptake of metals by wetlands would have continued through this period (Brown et al., 2000; Gossett et al., 1986).

Emissions began to fall with improvements in smelting techniques and regulations in the late 1970's leading to major reductions (> 95 % by the 2000s) (Meadows and Watmough, 2012). Pore water metal concentrations would have gradually decreased over this time period, and the equilibrium balance shifted in favour of the net release of metals from peat. By the late 1970's, the wetland-draining catchments had already become a net source of metals (see historical data on sites C1 and C2 in Chapter 2), and this has continued to present (Chapter 2). Plans are in place for a further 70-80 % reduction in metal emissions (Frank Javor, Vale, *personal*

communication), and wetlands in the area are likely to continue to be a source of metals for decades to come.

Summer droughts result in the short-term release of high concentrations of metals that can be potentially toxic (Chapters 3, 4), but may also lend to the depletion of metals from peats. Droughts have led to within-year variation of metal releases, and these events are becoming more prevalent in the boreal ecozone in general (see Trenberth, 2011). Summer drought conditions like that experienced in 2011 are relatively common in the Sudbury area, and 4 other years experienced lower rainfall and higher temperatures in the summer months than that which occurred in 2011 since 1960. This represents an average occurance every 9 years since 1975 (Figure 5.1). Both summer and annual mean temperatures are increasing quickly, and while annual rainfall has remained relatively consistent over the past 50 years with a slight upward trend, summer rainfall is trending downwards (Figure 5.1). These trends suggest an even higher frequency of occurance of these summer droughts in the future.

It has been suggested by Tipping et al. (2003) that bog peatlands in the U.K. are rapidly depleting of some metals, suggesting complete depletion within two or three drought events despite slower depletion of S pools. This is based on a model in which current metal inputs have declined and are unable to compensate for drought-related losses, and so while SO_4-related acidification may continue for longer, metal pools would rapidly deplete. The wetlands studied by Tipping et al (2003) are bogs with no input from uplands, whereas the upland soils in the Sudbury region remain contaminated and are likely an ongoing source of metal inputs to our poor fen wetlands (Meadows and Watmough, 2012). Furthermore, the deposition of metals in Sudbury is still higher than in the UK and elsewhere and Meadows and Watmough (2012) suggest that further emissions reductions are required to bring soil concentrations down below

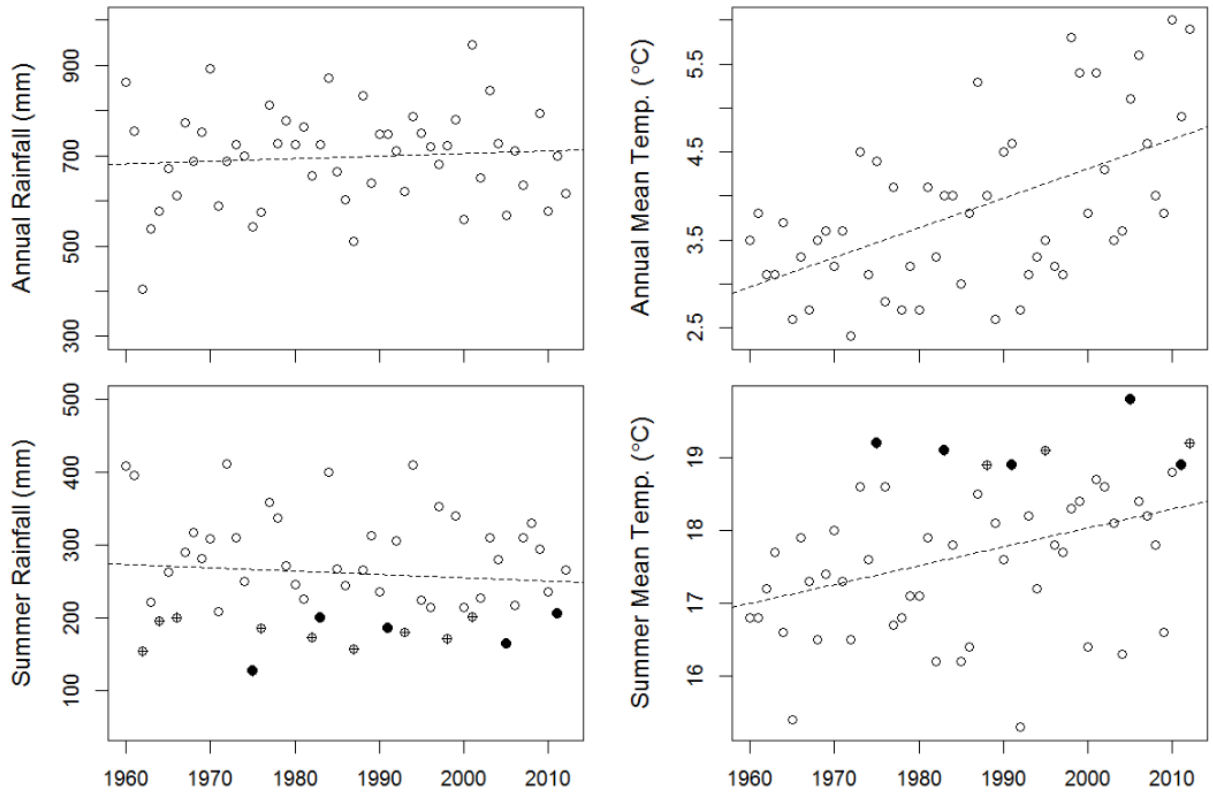

Figure 5.1: Total annual rainfall and mean temperature, and total summer rainfall and mean temperature recorded at the Sudbury Airport Environment Canada weather station from 1960 to 2012. Trends are shown with a dashed line, and years with lower summer rainfall or higher summer mean temperature as in 2011 are indicated with crossed points. Years where both lower rainfall and higher temperatures than 2011 occurred are indicated with closed points and occurred in 1975, 1983, 1991, and 2005. This represents an average occurance of "summer drought years" at least as severe as in 2011 every 9 years since 1975. Data is from Environment Canada (2014).

provincial guidelines. Higher depositional inputs coupled with upland contributions suggest that the depletion of metals from the poor fens in Sudbury will take much longer than for bogs in the UK as modelled by Tipping et al. (2003).

In contrast to the findings in the peat bogs of the U.K., work in a poor fen wetland in Southern Ontario suggests no substantial metal loss in relation to drought, and that it may take a very long time for metal stores to deplete (Adkinson et al., 2008). This Southern Ontario wetland (near

Dorset) is similar to the poor fen peatlands in this study, but has lower concentrations of metals. These lower peat metal pools will tend towards less release with equilibrium partitioning, and so losses may be of lower magnitude in these less contaminated sites where equilibrium is established with smaller pool sizes.

Studies have estimated that the depletion of upland soil metals in Sudbury will take decades or even centuries (Meadows and Watmough, 2012; Nriagu et al., 1998), and the time for depletion of metals in wetlands is likely of similar duration. Although an accurate estimate of the this depletion rate cannot be determined without quantification of upland and dry deposition inputs, a broad estimate can be made with the available data if we make the assumption that atmospheric deposition of metals will remain comparable to current levels. Given that water table fluctuations and oxidation is generally restricted to the upper 30 cm (Appendix A1, Reddy and DeLaune, 2008), this estimation is restricted to this upper "active layer" which has the greatest potential for release. In scenario A mass balances for this "active" layer are calculated assuming inputs to the wetlands are from deposition (Table 5.1). In scenario B mass balances for this "active" layer are calculated assuming inputs to the wetlands are from deposition as well as upland runoff (Table 5.1). This predictive model based on assumptions was repeated for Cu and Ni for both study years, and in all sites encompassing a range in metal and organic matter content.

From the results of this model, it is estimated that at best it will take many centuries to deplete Cu from these wetlands (scenario A), but that they may in fact still be gaining Cu (scenario B). The estimates also suggest that at best-case scenario the depletion of Ni from these wetlands would take as much as 100 years, with a longer estimated depletion at the site closest to the smelter (LU). The sites with thinner organic layers (D4 and D5) are estimated to deplete of metals more quickly than the other sites, with quickest depletion at the site with highest upland

Table 5.1: Estimated years to depletion of Cu and Ni pools in the study wetlands based on outflows measured in two study years (1: 2010 to 2011, 2: 2011 to 2012), and with inputs under two different input scenarios. Table continued on next page.

							A: Deposition			B: Deposition and Runoff		
	Catchment (m^2)	Wetland (m^2)	Metal Pool (kg)		Study year	Outflow (kg/yr)	Inputs (kg/yr)	Balance (kg/yr)	Years to Depletion	Inputs (kg/yr)	Balance (kg/yr)	Years to Depletion
C1	1002003	135464	Cu	3134	1	6.82	3.13	-3.69	849	23.15	16.3	gain
					2	5.24	1.37	-3.87	810	10.12	4.88	gain
			Ni	1938	1	20.8	1.28	-19.6	99	9.49	-11.4	170
					2	33.4	0.82	-32.6	59	6.03	-27.3	71
C2	274500	27659	Cu	533	1	1.77	0.58	-1.19	448	5.71	3.94	gain
					2	1.70	0.23	-1.47	363	2.30	0.60	gain
			Ni	467	1	3.68	0.24	-3.44	136	2.35	-1.33	351
					2	5.24	0.15	-5.10	91	1.45	-3.80	123
BR	268300	13832	Cu	358	1	1.42	0.17	-1.25	286	3.25	1.83	gain
					2	0.98	0.18	-0.79	453	3.54	2.56	gain
			Ni	300	1	4.83	0.18	-4.65	64	3.49	-1.34	224
					2	6.14	0.06	-6.09	49	1.13	-5.01	60

Metal pools are from Appendix A2, deposition data is from Appendix A4 and chapter 2, and outflow data is from appendix A4.

Table 5.1: Continued.

	Catchment (m^2)	Wetland (m^2)	Metal	Pool (kg)	Study year	Outflow (kg/yr)	A: Deposition Inputs (kg/yr)	A: Deposition Balance (kg/yr)	A: Deposition Years to Depletion	B: Deposition and Runoff Inputs (kg/yr)	B: Deposition and Runoff Balance (kg/yr)	B: Deposition and Runoff Years to Depletion
LU	109800	22868	Cu	798	1	1.26	0.46	-0.80	998	2.22	0.96	gain
					2	0.86	0.36	-0.51	1565	1.72	0.86	gain
			Ni	745	1	2.21	0.57	-1.64	454	2.73	0.53	gain
					2	5.33	0.15	-5.17	144	0.74	-4.59	162
D4	323900	4452	Cu	114	1	3.79	0.07	-3.72	31	4.96	1.17	gain
					2	1.78	0.03	-1.75	65	2.25	0.47	gain
			Ni	86	1	10.6	0.13	-10.5	8	9.26	-1.33	65
					2	8.81	0.01	-8.80	10	1.01	-7.80	11
D5	291500	4817	Cu	319	1	1.65	0.06	-1.58	202	3.91	2.26	gain
					2	1.12	0.03	-1.09	292	1.92	0.80	gain
			Ni	345	1	5.95	0.12	-10.5	33	7.23	1.28	gain
					2	9.44	0.02	-9.42	37	1.32	-8.13	42

Metal pools are from Appendix A2, deposition data is from Appendix A4 and chapter 2, and outflow data is from appendix A4.

influence (D4). In reality the upland contribution is likely to be somewhere between the two scenarios, but it is not unreasonable to assume that they are providing a large source of metals (more similar to scenario B) given that the catchments in the area are sparsely vegetated and have thin soils. Nriagu et al. (1998) suggest that Sudbury uplands have been saturated to the point that it may take centuries for the flux of elevated metals to subside. These scenarios of metal depletion are also likely to be largely underestimates because modelling was done in study years that were particularly dry. Although the summer drought occurred in 2011, the elevated concentrations from this drought happened largely in the preceeding fall, and is thus counted in the 2011-2012 budget that starts in October. So the estimated depletion rates from both study years may only occur under best case scenarios for metal release.

Cationic metals are tightly bound to peat and not easily released, and this is particularly true for metals such as Cu (Novak et al., 2011), which is why the depletion of these metals from the active layer is estimated to take a very long time. However, this surface layer of peat can be buried over time by the formation of new surface layers. This is a normal process in boreal peatlands, whereby fens slowly fill with peat and transition to bog peatlands (Reddy and DeLaune 2008). This could act to bury metals in deeper layers below the active surface layer as these peatlands naturally fill in, removing metals from the active layer where water table fluctuations occur. With this burial, the release of metals at high concentrations would be expected to decrease sooner than predicted, as metals would effectively be "removed" from the active layer of the wetland. The formation of peat is relatively slow, but surface layers can form quickly (Loisel and Garneau, 2010; van der Linden et al., 2014), with an estimated 20 cm forming in less than 50 years in some cases (Shotyk, 1996) but this varies between wetlands (Novak et al., 2011). However, ongoing work in the Sudbury area suggests that metal

concentrations in wetlands near the smelters are still higher close to the surface with peak concentrations at depths of only 5 to 7 cm (Sauter 2014), suggesting a very slow burial rate. This is likely a result of the relative absence of *Sphagnum* mosses in these wetlands (see Barrett 2014, and also discussed later), as they are the primary source of peat formation.

How Can We Mitigate the Release of Toxic Metals?

Given that metal loads will likely last a long time, the next question is: how can the magnitude of current metal releases be lessened to promote lower concentration releases that are less harmful to aquatic organisms? Wetlands retain metals through a variety of mechanisms including uptake by plants, reduction processes that result in metal precipitation, adsorption and exchange with organic matter functional groups (Gazea et al., 1996; Gambrell, 1994), and burial with the accumulation of peat over time (Shotyk, 1996). Boreal peatlands are characterized by high organic matter content and so exchange reactions with organic functional groups is a particularly important mechanism of metal retention. It was shown in chapters 3 and 4 that the largest release of these retained metals occurs in response to summer drought, with large fluxes of metals at high concentrations creating conditions that are potentially toxic to aquatic organisms. These conditions are exacerbated by drought-related changes in DOM composition that remove the binding capacity provided by aromatic sources of DOM. It is the oxidation of sulphur in peat facilitated by the loss of water and anoxic conditions that triggers these toxic releases, so it is necessary to increase the simultaneous retention potential of both water and metals within these wetlands and their catchments to lessen these toxic metal releases.

Influence of upland recovery and restoration

Extensive "regreening" programs have been ongoing in the Sudbury area since the mid 1970's, and over 3000 hectares had been limed, fertilized, and seeded by 1993, primarily along road corridors. Initial efforts to re-establish grasses, legumes, and deciduous trees (mostly birch, poplar, and willow primarily from wind-blown seed) were successful, and replanting of coniferous trees was quickly added to these ongoing restoration efforts (Lautenbach et al., 1995). This reclamation effort has promoted widespread recovery in the region, and the landscape now has much greater forest cover than it did in the past (Figure 5.2). Recent studies have suggested that land restoration programs should target watershed areas around lakes to promote the return of biodiversity and ecosystem function in terrestrial and aquatic systems simultaneously, as forests provide important organic subsidies to recovering lake communities (Tanentzap et al., 2014; Szkokan-Emilson et al., 2011; Wesolek et al., 2010). However, reforestation can result in increased evapotranspiration and reduced water yields in boreal catchments (Ellison et al., 2012; Buttle et al., 2000). This effect can be seen in the decreased runoff observed in catchments C1 and C2 since the 1970's (Table 2.6, Chapter 2), and land reclamation efforts must therefore consider these hydrologic effects in order to promote the supply and retention of water in lowland wetlands.

Although initial reforestation can increase evapotranspiration and reduce runoff, the water holding capacity of forest soils increases as forest stands mature (Elliott et al. 1998). Total annual runoff from mature forests is still lower than barren lands, but regulated released with less low-flow and high-flow variability throughout the seasons as well as shading that reduces surface evapotranspiration providing some buffer against summer droughts. This forest

Figure 5.2: Photographs taken at the same location over 20 years (at Martindale Hill) illustrating the regrowth of vegetation in the Sudbury area. From top left to bottom right, the photos were taken in 1985, 1995, and 2000 by K. Winterhalder, and in 2005 by P. Beckett.

regulation is strongest where soils are deep (Hinton et al., 1998; Devito et al., 1996), but it is likely to take thousands or even millions of years for these deep, mature soils to form (Targulian and Krasilnikov, 2007). Surface soils can form much quicker (Targulian and Krasilnikov, 2007) and these porous soils also play an important role in infiltration and slowing the flow of water (Bruijnzeel, 2004). The root systems of forest plants act to further enhance the infiltration of water into these surface layers, as well as slowing runoff and creating a more regulated release of water (Buttle et al., 2000; Buttle and House, 1997). The formation of surface soils may be accelerated by the natural "coppicing" of birch tree stands, whereby trees are continuously dying from stress and re-growing from the same root system, which rapidly produces new litter fall (Courtin, 1995). This coppicing and soil formation can be further accelerated by the managed felling and replanting of trees, and it is important that reforestation and land reclamation programs that promote rapid reestablishment of upland soils are considered.

Evapotranspiration-related decreases in annual water yield can also be lessened by selectively planting trees that uptake less water. For example, spruce plantations have lower evapotranspiration rates and retain more water in soil than natural pine forests (Elliott et al., 1998), and deciduous trees generally have lower evapotranspiration rates than coniferous trees (Ellison et al., 2012; Wattenbach et al., 2007). Hydrologic (BROOK90) models in small catchments suggest that conversion from coniferous to deciduous monocultures will result in increased soil water retention and annual discharge, primarily because of lower interception and vaporization (sublimation) back to the atmosphere of winter precipitation in deciduous forests (Armbruster et al., 2004). Current restoration efforts in Sudbury are aimed at bringing back a mixed forest, but it may be advisable to initially plant deciduous trees to maintain higher runoff and soil moisture content during the early years of forest succession, while in the long run

promoting the development of soil layers that will regulate flow and provide shade that cools surfaces, reduces evapotranspiration, and buffers against drought.

Water retention

Water from precipitation and upland runoff quickly flows over the surface of natural wetlands because organic substrates tend to have low permeability when saturated, resulting in little contact with metal-binding substrates. Slowing the flow of water not only increases contact with organic substrates but also promotes the retention of water in wetlands, buffering against water table declines and dry conditions. Constructed wetlands are often designed with subsurface inflows and distribution systems to increase contact time with organic soils and retention of water (Michelutti and Wiseman, 1995). While these flow patterns are not available in natural wetlands, slowed flows can be achieved by flow-control structures such as outflow weirs, but these are expensive to build and maintain. This may be a feasible option for individual projects but not as a large-scale, regional solution.

Beaver dams are also efficient at holding water, and the prolific flooding and associated biogeochemical and ecological changes that they can cause has led to beavers being referred to as "ecosystem engineers" (Wright et al., 2002). However their activity is sporadic and studies are varied on the effects of beaver impoundments on metal retention, with many showing little to no effect (Margolis et al., 2001; Smith et al., 1991). This is likely because impoundments are not restricted to wetlands and often flood forested areas where metal-binding peat is not initially abundant. Some benefit may be attained from limiting the harvest of beavers as they have been shown to promote wetland development at regional scales, but these are generally short-lived habitats (10 years or less) and once drained form meadows that can last for over 50 years

(Wright et al., 2002; Terwilliger and Pastor, 1999). A more controlled approach would be to promote the establishment of specific wetland plants that can slow the flow of water over the surface of existing wetlands (Lee and Scholz, 2007), increasing water retention, contact with organic substrates, and sedimentation of particulate-bound metals (Marchand et al., 2010).

Sphagnum mosses can retain as much as 27 times their dry weight in water (Crum, 1988; Hayward and Clymo, 1982), and Holden et al. (2008) found that *Sphagnum* mosses provided significantly greater hydraulic roughness and reduced surface flow compared to *Eriophorum* grasses, while mixed vegetation provided intermediate roughness and surface flow. *Sphagnum* can promote high water tables because their poor decomposition results in a buildup of porous material, providing a network to allow capillary rise throughout *Sphagnum* peat even if the water table is lowered, keeping upper peat layers wet (Goetz, 2014; Gignac and Beckett, 1986; Moore and Bellamy, 1974). Small precipitation events (<5 mm) can also temporarily increase *Sphagnum* water content equivalent to large increases in the water table, so intermittent rain events during drought can act to rewet surface layers (Strack and Price, 2009). This coupled with the high water retention capacity of live *Sphagnum* and the potential to slow surface flows suggests that these mosses can provide a buffer to water table changes and the oxidizing conditions of drought.

Sphagnum mosses are at uncharacteristically low abundance in Sudbury peatlands (Barrett, 2014), and although the exact cause is unclear there is evidence that they are sensitive to some smelter-related metals such as Cu and Zn (Tyler, 1990). The tolerances of *Sphagnum* mosses to metals are not well established and results in field experiments vary due to differences in biogeochemical conditions between sites (e.g.: pH, base cations) and species-specific differences (Tyler, 1990). In a survey of Sudbury-area wetlands in the early 1980s, Gignac and Beckett

(1986) noted a dominance of *Chamaedaphne calyculata* shrubs and a gradually increasing abundance of *Sphagnum* mosses with distance from the smelters (and decreasing Cu and Ni concentrations), with dominance in all surveyed peatlands beyond 30 km from the Copper Cliff smelter. Recent surveys have found similar patterns of increasing *Sphagnum* frequency with distance, with no *Sphagnum* species present at any sites surveyed within 8 km of the smelter (Barrett, 2014). Gignac and Beckett (1986) suggested that this lack of *Sphagnum* mosses created conditions favourable to increased drying. Further studies are required to determine the reason for the absence of *Sphagnum* mosses. These studies should include paleoecological investigations that could find associations between peat chemical conditions and the historical disappearance of *Sphagnum* mosses. Laboratory studies of metal tolearance are also needed, under conditions similar to Sudbury wetlands with a variety of interacting metals.

There is potential that the reintroduction of *Sphagnum* mosses may help to retain water in wetlands, however successful recolonization requires a relatively stable and high water table and soil moisture content to begin with (Price and Whitehead, 2004; Campeau and Rochefort, 1996), and may also be challenged by metal toxicity from peat stores as well as ongoing deposition (Tyler, 1990; Chapter 2). Severe or frequent desiccation can reduce productivity and survival of *Sphagnum* (McNeil & Waddington, 2003), so reintroductions may best be done during wet months and in particularly wet years. *Sphagnum* also appears to establish best where there are shrubs to offer protection from wind and erosion and to stabilise the peat surface (Campeau and Rochefort, 1996; Crum, 1988), and so it may be necessary to reintroduce shrubs concurrently with these mosses where absent. Once mosses are established, shrubs can act to further enhance the water retention capacity of *Sphagnum* mosses as reductions in surface wind and temperature reduce evaporative water losses from peat mats (Kuzovkina and Quigley, 2005). It is

recommended that trial reintroductions are performed under a variety of conditions to establish the best-case scenario for reestablishment. It is also recommended that a variety of *Sphagnum* species are explored, as some tend to show higher colonization success and tolerance to water table fluctuations than others, and this is success rate is likely region and/or site specific (Robroek et al., 2007; Campeau and Rochefort, 1996).

Metal retention

Not only do *Sphagnum* mosses increase water retention, but they are also able to efficiently adsorb metals and have been used to monitor airborne metal pollution (Vasconcelos and Tavares, 1998; Tyler, 1990; Little and Martin, 1974). It has been long-recognized that *Sphagnum*-dominated wetland systems can reduce aqueous metal concentrations and toxicity through metal adsorption reactions with both live mosses and the underlying peat (Dean et al., 2013; Weider and Lang, 1986). The exceptional ion exchange capacity of *Sphagnum* mosses and moss-derived peats was established as far back as in the 1950s, and this exchange capacity is a product of the high surface areas, numerous negatively charged exchange sites, and the highly absorbent nature of mosses (see review: Tyler, 1990). Furthermore, these mosses are resistant to degradation and so the small amount of DOM that is produced by *Sphagnum* mosses is highly bioavailable and less aromatic than that from other wetland plants (Gonzalez and Pokrovsky, 2014). The potential for DOC-related metal mobilization (i.e.: associated with the more aromatic forms) into surface waters is therefore reduced because the DOM is in a form that is quickly respired (Wickland et al., 2007).

Several other wetland plants have also been identified for their ability to uptake and retain metals and thus offer the potential for phytoextraction of metals, but this has been relatively poorly

studied for boreal-adapted plants. Herbaceous plants from the genera *Solidago* and *Thlaspi* have been shown to be hyperaccumulators of metals (Sheoran et al., 2009; Klang-Weston and Eriksson, 2003), but the North American species have not been well tested. It is recommended that shrubs be a target for local efforts instead, given the potential to also assist in the reestablishment of *Sphagnum* mosses. A good candidate for the area is *Salix* willows, as they have been found to hyperaccumulate metals (reviewed by Kuzovkina and Quigley, 2005) and are tolerant of acid conditions and nutrient-poor soils common to fen peatlands (Logan, 1992), so are commonly used in peat remediation projects (Kuzovkina and Quigley, 2005). While some species of *Salix* willows are more sensitive to water table decline than other shrubs (Amlin and Rood, 2002), they are generally tolerant of drying conditions (Kuzovkina and Quigley, 2005). Phytoextraction with willows can help to retain metals within peatlands and out of surface water, but also offers in some situations the possibility of regular harvesting of plant biomass to permanently remove metals from wetlands, a process called phytomining. Phytomining can in some cases even produce a product for further smelting, if metal concentrations are high enough for economic gain (Ali et al., 2013; Sheoran et al., 2009; Brooks et al., 1998).

Based on foliar chemistry, it appears that the wetlands in this study (and others in the Sudbury area) are P and K limited (Barrett et al., 2014). The addition of fertilizer might therefore assist in phytoremediation and phytomining by increasing plant biomass by orders of magnitude in wetland systems that are nutrient-limited (Sheoran et al., 2009; Li et al., 2003). Bennett et al. (1998) found that uptake of metals increased with fertilization of hyperaccumulators, and the uptake was due primarily to the increase in overall biomass rather than an increased uptake efficiency of individual plants. The addition of fertilizers and associated increases in plant biomass may also lead to accelerated peat formation, lending to quicker burial of peat metal

pools (Reddy and DeLaune, 2008). Furthermore, *Sphagnum* mosses are very efficient at uptake of nutrients and can out-compete other wetland plants in nutrient-poor systems. With fertilization, this competition is decreased and the co-occurrence of other species with *Sphagnum* increases (Malmer et al., 2003). Therefore it may be necessary to fertilize nutrient poor systems when considering the reintroduction of both *Sphagnum* mosses and *Salix* shrubs.

The recommendations provided here to alter or treat the wetland plants themselves may take time to produce positive outcomes. However, it is also possible to mitigate the release of metals into streams and receiving waterbodies through liming, achieving more immediate results while further mitigation strategies are established. The application of soluble dolomitic limestone can effectively increase the pH of wetland soils by supplying Ca and Mg which exchanges for protons and acidic aluminum cations in soil exchange sites (Gunn et al., 2001). Using peat from Sudbury peatlands including two study sites from this thesis (LU and D4), Juckers and Watmough (2014) found in a laboratory study that pH dropped by 0.5 units or more in response to 30 and 60 day simulated droughts regardless of pre-drought (baseline) pH, but that the final pH was related directly to this initial pH. This implies that if wetlands start out with higher pH, then the generation of protons and related metal releases in response to drought should be less. However, Juckers and Watmough (2014) noted variable metal releases in peat collected at different sites regardless of post-drought pH, likely because of differences in metal pool sizes, organic matter content, and base cation concentrations. Boreal peatlands are commonly acidic because of the presence of humic acids, but aerial application of limestone has successfully increased wetland pH and reduced metal release in Sudbury (Gunn et al., 2001) and elsewhere (Gonzalez-Alcaraz et al., 2013).

There may be a short-term risk with liming, in that the soil exchange sites will rapidly become saturated with Ca and Mg cations, and as such the solubility of some metals may temporarily increase. Gonzalez-Alcaraz et al. (2013) noted a liming-induced release of Cd and Mn in more mobilized fractions and attributed this to DOC-bound fractions, but the study was limited to a few weeks after application. Gunn et al. (2001) also noted an initial pulse in metal release with liming and attributed this to the exchange of base cations with bound metals, but this subsided after 4 or 5 weeks and was followed by lower concentrations of mobilized metals than before liming. This pulse was akin to the effect of a drought-related release, and should be considered when liming, because the effect may be to create temporary toxic conditions and to deplete the wetland metal pools more quickly. None-the-less, liming is likely to mitigate metal releases in response to drought conditions over the initial years of mitigation efforts, and may only be needed until further strategies can be implemented.

Selectively targeting wetlands for mitigation

There are over 33,000 ha of wetlands in the city of Greater Sudbury, many of which are connected to the 47,000 ha of lakes, rivers, and streams in the area (Monet, 2013). Managing these wetlands to mitigate metal releases is no small task, and requires identification of "locally significant" wetlands and those that may be at risk to drying. A Prioritization scheme is proposed whereby wetlands are placed into classes of importance (A, B, C), and then into subclasses of potential for impact (1, 2, 3) (Table 5.2). Class A (Highest priority) should be given to wetlands that are directly connected (via outflow streams) to "important" receiving waters (lakes or rivers). Important receiving waters could be drinking water sources (both main city intakes and were people draw for personal use) and/or those frequented for recreational use. Class B wetlands (medium priority) are those with direct connection to all other receiving waters, as they

Table 5.2: Proposed classification system for prioritizing locally significant wetlands for mitigation efforts in the Sudbury area.

Class: Importance	Subclass: Impact Potential
A Connected directly to receiving waters identified to be of high importance (e.g.: drinking water protection, recreational use, etc.).	**1** Wetlands in large watersheds with high upland disturbance (and near the smelters).
B Connected directly to any other receiving waters.	**2** Wetlands in small watersheds with high upland disturbance or large wetlands in watersheds with moderate upland disturbance.
C Not directly connected to any receiving waters.	**3** Wetlands in small watersheds and in areas of low upland disturbance.

Prioritization Ranking, highest to lowest: A1 > A2 > A3 or B1 > B2 > B3 > C

still pose risk to aquatic communities in those systems. Class C wetlands are lowest priority and are not directly connected to other receiving waters (e.g.: bog wetlands). Subclasses are proposed based on the probability for SO_4-mediated metal release. This is harder to assess, but should be based on proximity to smelters (as a proxy of impact) in that the wetlands closest to the smelter likely have larger metal pool sizes, less natural *Sphagnum* cover, and are exposed to ongoing deposition. Likelyhood for water table fluctuations should also be considered. Factors that affect water table fluctuation include depth of upland soil and upland vegetation cover (Buttle et al., 2000; Buttle and House, 1997), and size of watershed in that wetlands in large watersheds tend to experience larger water table fluctuations (Hill and Keddy, 1992). Subclass 1 (highest priority) should be wetlands that are in large watersheds in areas of high upland disturbance (for example see McCall et al., 1995), subclass 2 (medium priority) should be given to wetlands in small watersheds with high upland impact, or large watersheds with moderate upland impact, and

subclass 3 wetlands (lower priority) should be given to wetlands in small watersheds with minimal upland impact. Higher emphasis should be put on upland impacts rather than watershed size as the relationship between watershed size and water table fluctuations is not well established for small catchments (Hill and Keddy, 1992). This decision for wetland and watershed size criteria for division into subclasses can be facilitated with the use of remote sensing data and Geographic Information Systems (GIS) techniques based on the characteristics of the wetlands in the area, identifying all wetlands and separating them into classes. However, this classification system should be taken as a guideline for development of a more rigorous set of criteria.

Summary of Mitigation Recommendations

It is likely that it would take a very long time to deplete these wetlands of metal stores, and so some suggestions for mitigation strategies to lessen the release of these toxic metals have been provided. These recommendations are based on the retention of water in wetlands and entire catchments, and the retention of metals in peat and plant tissues within wetlands. Recovery of upland vegetation can lead to increased evapotranspiration and a reduction in water yield, and current restoration efforts in Sudbury are aimed at bringing back a mixed forest. It is advisable instead to initially plant deciduous trees to maintain higher runoff and soil moisture content during the early years of forest succession, while in the long run promoting the development of soil layers that will regulate flow and buffer against drought. The reintroduction of *Sphagnum* mosses and *Salix* willows to wetlands is also recommended, so as to slow the flow of water and increase retention of water and metals. *Salix* willows in particular offer the opportunity for phytomining as well, which can permanently remove metals from the wetlands. Fertilization of uplands may help to accelerate the production of biomass and litterfall, and fertilization of

wetlands may also help the production of new peat and the growth of *Salix* shrubs as well. This will ultimately lead to reductions in metal concentrations in the active surface layer of wetlands. Liming of target wetlands should also be considered to mitigate current drought-related metal releases, but should be considered as a temporary solution while further mitigation measures are implemented. Prioritization of wetlands for mitigation strategies can be based on the importance of the receiving waters that they drain into, as well as the potential for impact on those receiving waters.The development of detailed catchment model that takes into account upland processes, dry deposition and depositional changes through time, as well as wetland processes in a few representative watersheds is also recommended. This would provide a better estimate of the length of time required to deplete metal stores in these wetlands, and help to weigh the costs of mitigation strategies versus long term benefits.

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A. Appendices

A1. Regional Survey of Sudbury Wetlands

A preliminary survey of annual water table fluctuation in 29 wetlands was conducted in the region in 2010. Five 1 m long stakes with red electrical tape attached along the length were installed into each wetland to record maximum and minimum water table heights over a year (from July 2010 to July 2011). The stakes were installed throughout the wetland area and results were used to estimate total fluctuation (difference from highest to lowest water table heights) as well as maximum and minimum heights relative to soil surface. This was done following the methods of Belyea (1999) (modified from Bragazza, 1996; Stephenson et al., 1994), whereby hydrogen sulphide reacts in reduced conditions to discolour PVC tape. Belyea (1999) note that the change in colour could be a result of either reduction of Fe^{3+} to Fe^{2+} (or other metals) or chemical reaction of hydrogen sulphide with metals to produce a deposit (e.g. iron sulphide). Although 5 stakes were installed in all wetlands, several were lost or damaged, and so the final number of stakes in a given wetland varied from 1 to 5. There were a total of 104 stakes retreived, and the average fluctuation and minimum and maximum water table heights were recorded (Table A.1).

Peat samples were collected from a subset of 18 of the wetlands (primarily poor or transitional fens) revealing a range in metal and nutrient content, and vegetation surveys were conducted on this subset as well (See Barrett 2014) (Table A.2)

Table A.1: Maximum and minimum water table heights as well as mean fluctuation recorded across all stakes in each of the 29 wetlands in Sudbury, Ontario. Coordinates are given in standard NAD83 UTM format, zone 17N.

Site	Northing	Easting	Number of Stakes	Min. (cm)	Max. (cm)	Mean Fluctuation (cm)
BR	5137984	502533	4	-11.5	14.0	13.8
LIV1	5142897	488608	1	7.5	16.0	8.50
SLV	5142026	498683	4	-38.0	16.3	24.5
LON	5135089	494876	3	-17.0	17.0	19.3
C1	5134720	496181	5	-10.5	16.5	19.2
FAIRBN	5147099	468614	4	-24.5	19.0	35.7
CRO2	5136790	502598	5	-17.0	5.5	17.1
CRO1	5137251	502017	4	-11.5	8.0	14.9
WHT1	5159656	500660	5	-9.5	23.5	13.9
WNDY1	5161455	464348	2	-14.5	25.5	34.5
MUD	5144547	487312	2	-39.5	17.0	42.8
LIV2	5144539	485876	4	-10.0	16.5	20.4
RCK	5174862	505603	5	-25.0	8.5	12.7
CAP1	5172946	508339	4	-38.0	20.0	39.8
RADRD	5163718	513121	5	-12.5	21.0	14.8
KUK1	5153949	527423	2	-57.5	16.5	42.2
KUK2	5167812	528131	1	-26.2	11.7	37.9
MAT	5173379	529092	4	-17.2	15.7	22.9
ASH	5165870	529515	5	-47.2	-8.0	35.8
LU	5144602	502543	5	-16.4	18.7	16.6
LU2	5144898	502775	2	-5.1	19.5	23.5
H17	5146964	509351	3	-9.0	15.0	19.7
FORLK	5169881	499201	5	-53.0	8.5	51.3
NELLK	5170895	493032	4	-36.0	19.5	46.0
D2	5145499	508885	4	-23.0	7.6	19.4
D4	5144593	509036	3	-19.6	17.2	21.3
D5	5144446	508502	3	-13.5	11.0	16.5
MOX	5141194	493489	5	-39.0	21.2	25.8
WHN	5141704	520126	1	-32.5	-8.5	24.0
Total			***104***	***-23.0***	***14.1***	***24.2***

Table A.2: Means, standard deviations, maximums and minimum concentrations of metals, cations, nutrients, pH, and von Post humification index from the top 15 cm of peat in 18 Sudbury wetlands. Table from Barrett (2014). These 18 sites include the 6 from this study.

	Surface Peat (0-15 cm)			
Variables	Average	±SD	Max	Min
Na g kg^{-1}	0.61	0.19	1.24	0.34
K g kg^{-1}	0.75	0.19	1.12	0.55
Ca g kg^{-1}	3.38	1.81	7.10	0.72
Mg g kg^{-1}	0.77	0.53	2.31	0.33
P mg/kg	780	187	1116	466
Al g kg^{-1}	7.65	5.22	21.0	1.72
Fe g kg^{-1}	7.04	3.91	17.3	3.09
Mn mg kg^{-1}	56.9	35.0	147.2	18.2
Ni mg kg^{-1}	521	221	920	120
Cu mg kg^{-1}	890	420	1685	169
Co mg kg^{-1}	12.0	3.35	20.5	5.59
Zn mg kg^{-1}	48.5	15.9	81.2	17.0
%N	1.88	0.46	2.50	0.71
%C	40.5	12.0	51.1	12.1
%S	0.71	0.26	1.25	0.22
CN Ratio	21.8	5.40	31.9	12.9
pH	3.95	0.35	4.48	3.31
von Post	H4	1.3	H8	H2

A2. Peat Chemistry and Pool Sizes

Peat samples were collected in 2012 at five stations in each wetland and from two depths: 0 to 15 cm and 15 to 30 cm. The peat was digested with trace grade HNO_3 at 100 ^oC for 8 hours and diluted with MilliQ water to 2 % HNO_3. Analysis was done with a PerkinElmer Optima 7000DV ICP-OES (Al, Ca, Co, Cu, Fe, K, Mg, Mn, Ni, P, Zn) and an ELEMENTAR combustor for % C, N, and S. NIST-1515-SRM apple leaves were included to verify accuracy and precision, and recoveries ranged from 85 to 98 %. Peat data were obtained from Barrett (2014) and Pennington (2014) (Table A.3). Pool sizes were estimated for metals using the mean concentrations and bulk densities of each layer (Table A.4).

Table A.3: Mean (SD) concentrations (mg/kg) of metals, cations, bulk density, and nutrient content (%) in the surface (0 to 15 cm) peat layer of six wetlands.

	C1		C2		BR		LU		D4		D5	
Bulk Density (g/cm^3)	*0.172*	*(0.045)*	*0.172*	*(0.028)*	*0.146*	*(0.023)*	*0.165*	*(0.028)*	*0.172*	*(0.057)*	*0.787*	*(0.456)*
Al	5345	(1738)	1716	(50.8)	10456	(2589)	3356	(777)	20950	(4503)	18618	(2683)
Co	9.35	(3.32)	8.36	(0.200)	10.4	(0.888)	17.3	(4.35)	11.8	(1.52)	12.0	(1.57)
Cu	844	(179)	635	(83.3)	1039	(143)	1238	(428)	711	(183)	512	(116)
Fe	7656	(2660)	8179	(2177)	3091	(108)	7866	(733)	15290	(812)	17272	(4137)
Mn	39.2	(5.88)	29.1	(0.590)	42.5	(7.75)	47.1	(13.8)	62.5	(22.6)	92.4	(12.8)
Ni	472	(193)	348	(11.2)	540	(47.2)	920	(231)	275	(47.2)	429	(186)
Zn	42.9	(15.7)	38.7	(8.08)	43.0	(12.6)	64.7	(20.2)	41.3	(14.0)	45.2	(2.14)
Na	507	(106)	705	(84.0)	572	(57.2)	1245	(336)	491	(194)	468	(28.2)
K	674	(96.1)	834	(240)	591	(61.2)	1019	(171)	1044	(399)	1117	(197)
Ca	2524	(603)	5432	(1043)	1741	(294)	5837	(2326)	723	(159)	1727	(403)
Mg	586	(127)	385	(13.5)	384	(42.9)	403	(68.6)	1721	(978)	2315	(533)
% C	31.8	(4.34)	48.4	(1.24)	39.6	(2.28)	49.2	(0.490)	17.3	(3.40)	12.1	(5.83)
% N	1.31	(1.04)	1.73	(0.234)	2.11	(0.204)	1.86	(0.230)	1.34	(0.212)	0.713	(0.260)
% S	0.390	(0.339)	0.695	(0.159)	0.756	(0.093)	0.675	(0.094)	0.238	(0.065)	0.224	(0.103)

Table A.3: Continued: Lower peat layer (15 to 30 cm).

	C1		C2		BR		LU		D4		D5	
Bulk Density (g/cm^3)	*0.290*	*(0.016)*	*0.274*	*(0.070)*	*0.192*	*(0.029)*	*0.329*	*(0.066)*	*0.299*	*(0.061)*	*1.52*	*(0.051)*
Al	16792	(11304)	2563	(524)	15565	(2760)	5329	(429)	45871	(7554)	14510	(2327)
Co	22.0	(6.14)	4.98	(1.24)	11.0	(5.17)	19.4	(8.14)	31.6	(6.71)	13.8	(3.45)
Cu	31.3	(25.6)	70.6	(35.0)	108	(28.0)	86.4	(44.3)	160	(90.5)	25.1	(9.57)
Fe	8498	(3764)	1678	(495)	1901	(410)	2553	(271)	34475	(6362)	14442	(634)
Mn	65.5	(11.7)	24.7	(6.17)	109	(28.4)	54.1	(11.2)	588	(286)	164	(52.4)
Ni	49.0	(40.6)	192	(58.8)	342	(194)	199	(71.9)	271	(148)	91.6	(60.0)
Zn	5.08	(2.02)	26.3	(4.30)	41.8	(30.8)	15.2	(9.62)	156	(26.9)	46.9	(9.03)
Na	627	(50.9)	617	(23.1)	369	(158)	426	(106)	606	(44.4)	556	(27.4)
K	622	(303)	193	(55.4)	153	(40.9)	92.4	(26.0)	3266	(581)	965	(114)
Ca	3185	(1208)	3407	(499)	5875	(1459)	10652	(1790)	2592	(1644)	1348	(304)
Mg	1867	(508)	302	(75.6)	673	(131)	715	(138)	7570	(1245)	3995	(289)
% C	3.63	(4.73)	51.6	(1.79)	40.2	(4.26)	51.5	(0.82)	5.58	(1.44)	3.30	(2.45)
% N	0.215	(0.245)	1.58	(0.219)	2.00	(0.150)	1.80	(0.118)	0.425	(0.105)	0.202	(0.147)
% S	0.058	(0.049)	0.442	(0.142)	0.597	(0.077)	0.428	(0.049)	0.095	(0.019)	0.167	(0.152)

Table A.4: Estimated pool sizes of nutrients, metals, and other cations in surface (0 to 15 cm) and the lower layer (15 to 30 cm) of peat in the six wetlands.

	C1	C2	BR	LU	D4	D5
Surface Layer (0 to 15 cm)						
Al	1379	443	2290	831	5405	21979
Co	2.41	2.16	2.28	4.28	3.04	14.2
Cu	218	164	228	306	183	604
Fe	1975	2110	677	1947	3945	20390
Mn	10.1	7.51	9.31	11.7	16.1	109
Ni	122	89.784	118	228	70.95	506
Zn	11.1	9.98	9.42	16.0	10.7	53.4
Na	131	182	125	308	127	552
K	174	215	129	252	269	1319
Ca	651	1401	381	1445	187	2039
Mg	151	99.33	84.1	99.7	444	2733
% C	82044	124872	86724	121770	44634	142841
% N	3380	4463	4621	4604	3457	8417
% S	1006	1793	1656	1671	614	2644
Lower Layer (0 to 30 cm)						
Al	7305	1053	4483	2630	20573	33083
Co	9.57	2.05	3.17	9.57	14.2	31.5
Cu	13.6	29.0	31.1	42.6	71.8	57.2
Fe	3697	690	547	1260	15462	32928
Mn	28.5	10.2	31.4	26.7	264	374
Ni	21.3	78.9	98.5	98.2	122	209
Zn	2.21	10.8	12.0	7.50	70.0	107
Na	273	254	106	210	272	1268
K	271	79.3	44.1	45.6	1465	2200
Ca	1385	1400	1692	5257	1163	3073
Mg	812	124	194	353	3395	9109
% C	15791	212076	115776	254153	25026	75240
% N	935	6494	5760	8883	1906	4606
% S	252	1817	1719	2112	426	3808

A3. Hydrologic Modelling Methods

Rating curves

HOBO™ U20 pressure-based water level loggers were setup up in each stream behind a natural control structure. Stream water levels were recorded at 15 minute intervals from October 2010 to October 2012 (excluding winter months: December to March) and calibrated to 1m staff gauges installed adjacent to the loggers. Stream flow was measured 11 to 14 times at each site from April 2011 to June 2012 across a range of water heights over two years using a Marsh-McBirney Flo-Mate™ 2000 velocity meter. Total sampling events were limited, occurring primarily in spring and fall, because of low flow and drought conditions in summer months (Table A.5). Total discharge for the sampling event was taken as an average of two replicate measures taken in the field, and stream water height at the sampling event was extracted from the nearest 15 minute HOBO™ U20 logger reading. A power relationship between flow (Q) and height (h) was established with the formula

$$Q = C\,(h + a)^{b}$$

where a is the height of zero flow (Q), b is the calculated power exponent, and C is a calculated coefficient corresponding to the station. All of the sites except LU had exponents (b) in the range characteristic of rectangular to parabolic stream beds (1.6 to 3.0), and LU had an exponent above 3, characteristic of an irregularly shaped stream or a floodplain channel (Figure A.1). This is expected for LU as the channel is deeper than it is wide and it occasionally floods over the banks (Terzi, 1981). Despite the limited sampling as a result of drought events, successful relationships between Q and h were established yielding R^2 values of 0.95, 0.95, 0.92, 0.94, 0.98, and 0.99 for C1, C2, D4, D5, BR, and LU respectively (Figure A.1). These relationships allowed for

estimation of flow for every 15 minute interval of measured height, for summation to daily totals.

Winter flows

Flows could not be estimated using traditional rating curve methods during the ice-covered months (December to March), so a regional winter flow model was generated using the BROOK 90 v4.5 hydrologic model (Federer, 2002). This model makes use of the following daily meteorological data to estimate flow: solar radiation (MJ/m^2), minimum and maximum temperatures (^oC), mean vapour pressure (kPa), wind speed (m/s), precipitation (mm), and measured discharge data (where available) (mm). Daily data was retrieved from the Sudbury Airport Environment Canada weather station. Solar radiation data was not available from this station, and so an estimate was calculated from cloud cover data at the Muskoka Airport Environment Canada weather station. Site C2 was used as the modelled catchment, as it had intermediate wetland size and total watershed area. All modelling was done with the assistance of Dr. Huaxia Yao, Hydrology and Meteorology Scientist at the Dorset Environmental Science Centre, as he has extensive experience with calibrating this model. Modelled flow was compared to measured flow at C2 and Nash-Sutcliffe coefficients of efficiency (NSE) of 0.59 and 0.69 were obtained for daily and monthly data respectively, above the suitable cut-off of 0.5 suggested by Moriasi et al. (2007) for adequately replicated observations. Modelled flow was prorated to the other five catchments by watershed area for use in place of missing winter flow, as all of the catchments behave similarly (Figure A.2).

Table A.5: Stage and discharge measures at the six wetland-draining streams taken between April 2011 and June 2012. Table continued on the next page.

Site	Date	Stage	Discharge	a
C1	2011-04-07	0.299	35.6	-0.09
	2011-04-12	0.347	76.0	
	2011-04-28	0.462	269	
	2011-04-29	0.384	120	
	2011-05-12	0.176	6.73	
	2011-11-04	0.210	6.23	
	2011-11-23	0.194	3.00	
	2012-04-13	0.148	1.63	
	2012-05-11	0.164	0.901	
	2012-05-17	0.138	0.360	
	2012-06-04	0.218	5.02	
C2	2011-04-08	0.188	10.3	-0.04
	2011-04-12	0.208	14.9	
	2011-04-28	0.308	73.4	
	2011-04-29	0.246	34.9	
	2011-05-12	0.080	0.938	
	2011-10-21	0.230	9.76	
	2011-10-27	0.108	1.21	
	2011-11-04	0.108	1.93	
	2011-11-23	0.092	0.510	
	2012-04-13	0.064	0.107	
	2012-04-27	0.158	2.77	
	2012-05-11	0.062	0.044	
BR	2011-04-07	0.251	11.5	-0.1
	2011-04-12	0.249	17.8	
	2011-04-28	0.386	68.5	
	2011-04-29	0.282	27.8	
	2011-05-12	0.168	2.44	
	2011-10-21	0.238	11.2	
	2011-10-27	0.170	2.52	
	2011-11-04	0.178	2.75	
	2011-11-23	0.168	1.52	
	2012-04-15	0.196	0.294	
	2012-04-27	0.246	2.00	
	2012-05-11	0.208	0.529	
	2012-05-30	0.188	0.114	
	2012-06-04	0.230	1.38	

Table A.5: Continued.

Site	Date	Stage	Discharge	a
LU	2011-04-07	0.230	10.8	0
	2011-04-12	0.206	5.24	
	2011-04-28	0.312	28.5	
	2011-04-29	0.249	13.9	
	2011-05-12	0.090	0.246	
	2011-10-24	0.162	1.84	
	2011-10-27	0.138	0.759	
	2011-11-04	0.134	0.602	
	2011-11-23	0.102	0.264	
	2012-04-15	0.064	0.050	
	2012-04-26	0.146	0.901	
	2012-05-10	0.058	0.028	
	2012-05-16	0.088	0.224	
D4	2011-04-07	0.271	10.2	-0.07
	2011-04-12	0.270	8.80	
	2011-04-28	0.457	209	
	2011-04-29	0.323	25.3	
	2011-10-19	0.118	0.192	
	2011-10-27	0.155	2.19	
	2011-11-02	0.123	0.658	
	2011-11-16	0.141	1.16	
	2012-04-15	0.111	0.319	
	2012-04-26	0.173	2.22	
	2012-05-10	0.124	0.248	
	2012-05-16	0.111	0.043	
	2012-06-04	0.149	0.355	
D5	2011-04-07	0.184	12.5	-0.123
	2011-04-12	0.187	12.3	
	2011-04-28	0.448	124	
	2011-04-29	0.270	40.1	
	2011-05-12	0.146	2.78	
	2011-10-19	0.124	0.000	
	2011-10-27	0.155	1.65	
	2011-11-02	0.140	0.940	
	2011-11-16	0.162	2.00	
	2012-04-15	0.138	0.744	
	2012-05-10	0.152	0.643	
	2012-05-16	0.144	0.463	
	2012-05-30	0.132	0.376	
	2012-06-04	0.138	0.618	

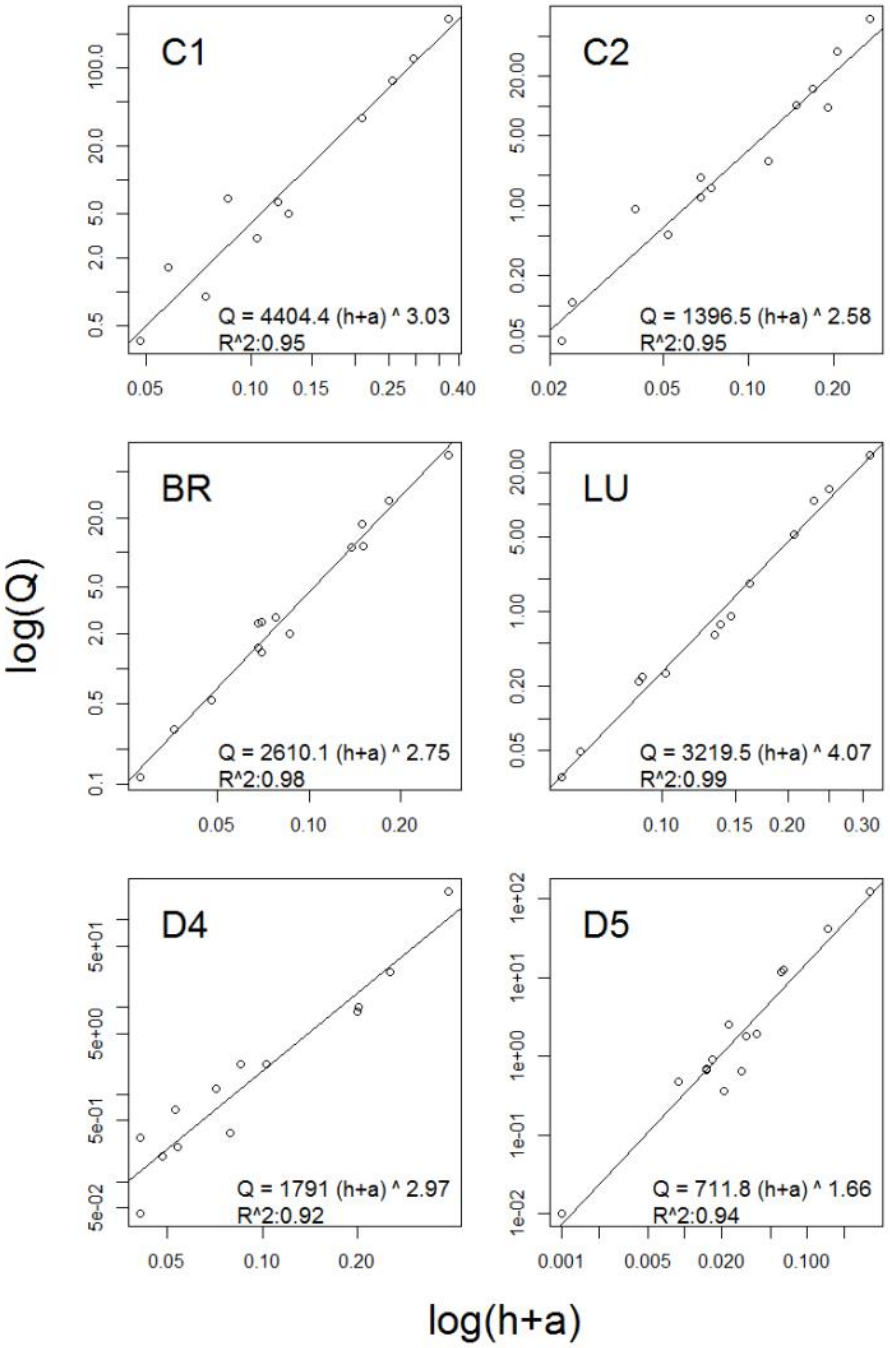

Figure A.1: Stage (h+a) discharge (Q) rating curves for the six wetland draining streams, with each axis on in logarithmic scales. The power equation and R^2 are indicated. Note: h is the recorded height on the staff gauge, and a is height at 0 flow.

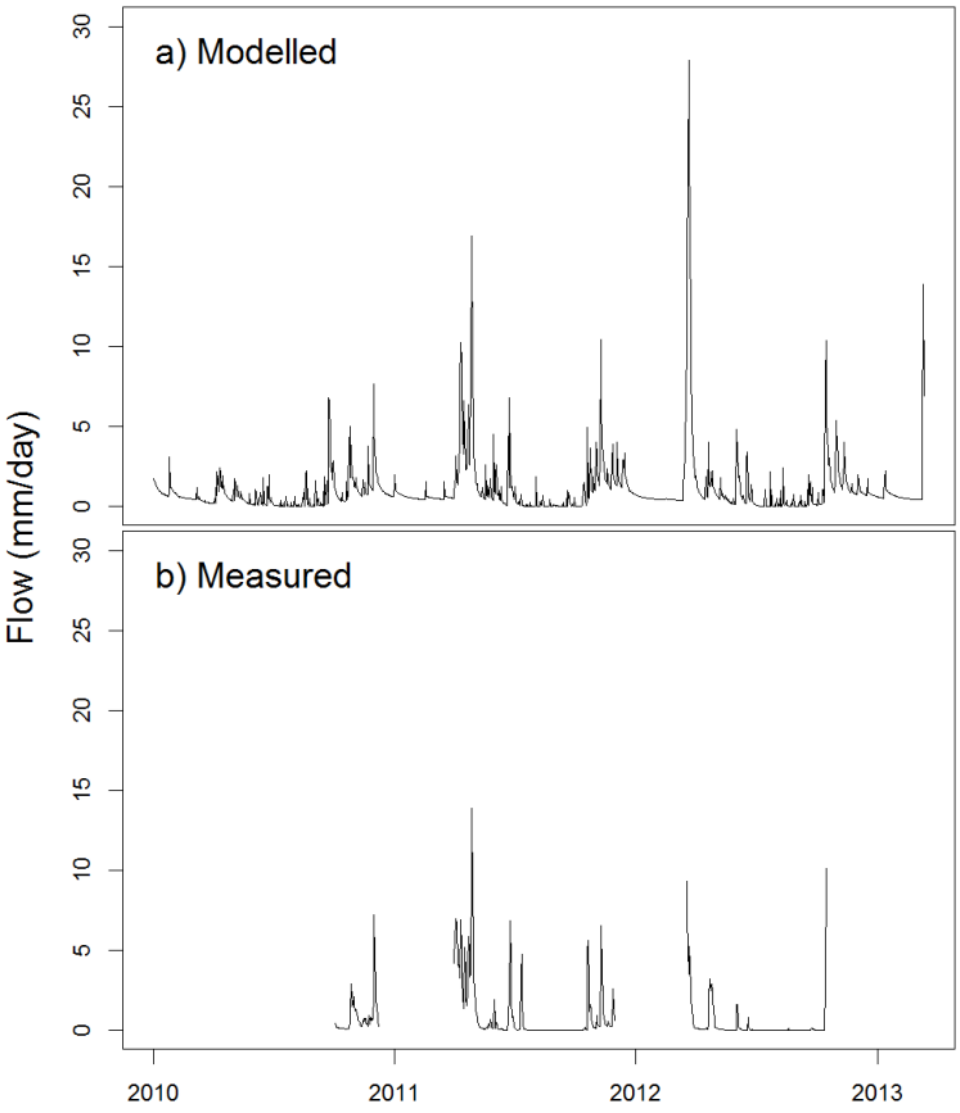

Figure A.2: BROOK 90 modelled flow (a) versus rating-curve measured flow (b) from January 2010 to March 2013 in site C2, standardized by watershed area (mm/day). Modelled data is used in place of missing flow during winter months.

A4. Catchment Budget Calculations

Stream flow was estimated every 15 minutes (see Appendix A3) and summed to a total daily volume. Daily chemistry values were obtained from samples taken every 2 to 4 weeks, using the midpoint method to infill days without samples. This method was done such that the last collected sample was carried forward for each consecutive day until the midpoint between collections, and the next sample was carried back to the midpoint. If there was an odd number of infilled day then the midpoint value was taken as the average of the two carried values (Eimers et al., 2008). Daily stream outflow fluxes were then calculated as the product of daily outflow volume and daily concentrations, repeated for sulphate, and all metals and other cations, and summed to monthly totals weighted by catchment area (Table A.6).

Bulk atmospheric deposition was collected at each catchment in samplers constructed of 30.5 cm diameter polyethylene funnels draining into polyethylene bags through 80 μm Nitex filters, and placed 1 m above the ground in the middle of the wetland. Winter deposition was collected in a polyethylene bag in a 35 cm deep open bucket (30.5 cm diameter), and thawed and filtered through an 80 μm Nitex filter. Deposition volume was measured and a 300 ml subsample was kept for analyses. The loss of a sample was rare, but values from the nearest neighbouring collector were used when it occurred. Bulk deposition fluxes were calculated as the product of the concentration and volume collected for the collection period, usually 2 or 4 weeks depending on rain events and availability of water (Table A.7).

Input and outflow fluxes were then summed to annual totals for the two sampling years, and weighted by catchment area. Annual catchment budgets were calculated from October to September of each year by subtraction of total annual catchment outflow from total annual

deposition inputs (note that the 2011 to 2012 budget was calculated annually to Oct. 15 due to sampling delay) (Table A.8).

Table A.6: Monthly catchment-weighted (mg/m^2) outflow fluxes of metals, cations, and sulphate in the six catchments and for both budget years. Note that budgets end on October 15, 2012 (due to sampling delay). Table continued on the next 5 pages.

Site	Year	Month	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
C1	2010	Oct	7.05	2.28	27.7	0.051	0.236	11.6	2.64	9.55	0.740	12.1	1.11	38	0.097
	2010	Nov	10.4	2.72	37.8	0.083	0.223	6.89	3.66	13.9	1.06	16.3	1.47	61	0.121
	2010	Dec	42.8	9.43	138	0.343	0.604	3.86	13.3	56.1	4.09	60.8	5.35	265	0.418
	2011	Jan	23.2	5.49	72.7	0.180	0.362	3.31	7.84	28.6	2.20	32.6	2.78	144	0.220
	2011	Feb	16.0	7.38	28.9	0.070	0.566	13.6	11.4	2.25	1.39	18.8	0.815	97	0.089
	2011	Mar	18.1	8.33	32.6	0.079	0.639	15.4	12.9	2.53	1.57	21.2	0.920	110	0.101
	2011	Apr	156	47.8	260	0.477	3.09	53.6	98.6	99.1	10.7	185	6.08	386	1.85
	2011	May	17.1	5.20	27.5	0.050	0.406	7.48	12.8	10.3	0.904	19.5	0.891	29.9	0.119
	2011	Jun	9.80	3.11	13.9	0.034	0.409	19.4	4.34	4.95	0.525	14.3	0.745	3.9	0.065
	2011	Jul	6.89	2.19	9.82	0.025	0.277	14.5	2.89	3.42	0.384	9.89	0.624	2.75	0.046
	2011	Aug	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2011	Sep	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.003	0.000
	Total:		*307*	*93.94*	*650*	*1.39*	*6.81*	*150*	*170*	*231*	*23.6*	*391*	*20.8*	*1137*	*3.13*
C1	2011	Oct	22.6	7.10	131	0.297	0.546	5.38	32.5	47.3	3.65	37.4	5.07	188	0.871
	2011	Nov	36.0	9.46	147	0.338	0.686	4.40	13.4	53.8	4.09	60.0	7.80	217	0.892
	2011	Dec	50.9	12.0	178	0.380	1.15	8.97	16.0	64.6	4.75	102	8.45	247	0.777
	2012	Jan	18.1	3.68	73.9	0.153	0.413	4.84	5.97	26.5	2.02	43.8	2.79	77	0.331
	2012	Feb	13.1	2.58	35.1	0.051	0.304	3.59	17.5	12.9	0.931	24.4	1.47	49	0.267
	2012	Mar	63.0	8.60	85.1	0.151	1.17	11.1	33.5	30.0	4.00	60.8	4.10	118	0.496
	2012	Apr	21.0	3.24	38.9	0.059	0.458	2.39	7.59	13.1	0.947	32.9	1.78	51	0.331
	2012	May	5.04	0.762	8.29	0.019	0.132	0.919	1.89	3.00	0.200	8.48	0.366	10.4	0.021
	2012	Jun	4.36	0.926	6.52	0.012	0.186	2.91	0.498	2.48	0.177	6.81	0.334	1.72	0.000
	2012	Jul	0.00	0.000	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2012	Aug	0.269	0.056	2.71	0.002	0.012	0.132	0.317	0.820	0.055	2.04	0.029	1.29	0.009
	2012	Sep	0.631	0.184	2.32	0.006	0.017	0.159	0.810	0.909	0.072	0.984	0.120	3.8	0.017
	2012	Oct	5.49	1.60	20.2	0.049	0.150	1.38	7.05	7.91	0.626	8.56	1.04	32.9	0.145
	Total:		*240*	*50.2*	*729*	*1.52*	*5.23*	*46.1*	*137*	*263*	*21.5*	*388*	*33.3*	*996*	*4.16*

Table A.6: Continued.

Site	Year	Month	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO4-S	Zn
C2	2010	Oct	14.9	4.00	199	0.067	0.405	9.81	15.5	33.5	0.853	160	1.34	91	0.329
	2010	Nov	21.9	5.41	301	0.101	0.493	8.36	22.0	50.7	1.01	238	1.55	134	0.476
	2010	Dec	42.6	8.96	583	0.192	0.739	6.40	40.5	98.5	1.37	449	2.20	254	0.875
	2011	Jan	22.3	4.76	297	0.098	0.389	3.70	21.3	48.3	0.726	236	1.11	130	0.446
	2011	Feb	15.4	4.00	135	0.049	0.295	5.85	15.9	3.54	0.578	180	0.402	62	0.204
	2011	Mar	17.4	4.52	153	0.055	0.332	6.60	17.9	4.00	0.652	203	0.453	70	0.231
	2011	Apr	149	47.5	934	0.387	2.93	63.1	147	130	6.622	1056	3.807	397	2.67
	2011	May	16.3	5.45	135	0.045	0.352	5.08	17.9	22.0	0.610	135	0.789	37	0.307
	2011	Jun	23.8	2.72	164	0.055	0.353	3.31	12.9	22.9	0.545	183	1.25	30.7	0.360
	2011	Jul	11.8	1.12	53.3	0.020	0.160	1.46	5.16	7.22	0.190	67.9	0.479	14.1	0.159
	2011	Aug	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2011	Sep	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Total:		*335*	*88.4*	*2955*	*1.07*	*6.44*	*114*	*316*	*420*	*13.2*	*2910*	*13.4*	*1219*	*6.06*
C2	2011	Oct	20.1	7.39	287	0.120	0.494	7.11	35.3	36.1	1.22	160	0.800	124	0.914
	2011	Nov	33.9	9.34	446	0.147	0.787	7.27	32.9	68.9	1.04	321	3.86	177	1.44
	2011	Dec	48.8	16.0	567	0.203	1.48	21.9	35.2	88.1	1.22	478	4.76	215	1.87
	2012	Jan	17.4	7.49	248	0.062	0.572	18.1	13.9	37.9	0.442	182	1.76	86	1.14
	2012	Feb	12.5	2.26	156	0.029	0.317	2.18	8.29	18.8	0.200	148	1.16	53	0.496
	2012	Mar	58.0	13.2	327	0.163	1.49	20.4	77.2	51.2	2.23	383	3.35	126	1.09
	2012	Apr	22.1	4.32	210	0.052	0.508	3.86	15.6	30.9	0.328	212	1.79	58	0.725
	2012	May	0.947	0.176	9.10	0.002	0.024	0.160	0.622	1.39	0.014	9.37	0.074	2.53	0.019
	2012	Jun	5.78	1.08	74.5	0.022	0.164	0.949	1.84	11.3	0.141	68.2	0.572	2.48	0.131
	2012	Jul	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2012	Aug	0.125	0.045	1.29	0.000	0.005	0.062	0.200	0.219	0.006	0.966	0.013	0.62	0.005
	2012	Sep	0.501	0.178	5.18	0.000	0.021	0.249	0.802	0.877	0.024	3.87	0.054	2.47	0.021
	2012	Oct	8.05	2.86	83.2	0.000	0.335	3.99	12.9	14.1	0.387	62.1	0.867	40	0.343
	Total:		*228*	*64.3*	*2415*	*0.802*	*6.20*	*86.2*	*235*	*360*	*7.25*	*2029*	*19.1*	*887*	*8.19*

Table A.6: Continued.

Site	Year	Month	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
BR	2010	Oct	4.29	1.55	16.1	0.042	0.100	5.15	1.73	5.28	0.627	6.19	0.666	22.4	0.054
	2010	Nov	7.44	2.48	26.5	0.077	0.124	4.32	3.09	9.06	1.14	9.09	1.05	39	0.082
	2010	Dec	40.1	11.6	134	0.413	0.383	2.00	16.0	46.5	4.99	42.1	4.62	209	0.351
	2011	Jan	22.3	6.42	73.6	0.222	0.232	1.44	9.26	24.4	2.70	23.3	2.47	113	0.191
	2011	Feb	15.4	4.00	42.4	0.085	0.334	4.00	9.55	3.08	1.13	14.6	0.798	47	0.089
	2011	Mar	17.4	4.52	47.8	0.095	0.377	4.52	10.8	3.48	1.27	16.5	0.900	53	0.100
	2011	Apr	141	45.9	286	0.771	2.86	34.7	88.9	88.9	11.5	177	4.86	411	1.97
	2011	May	28.8	6.58	33.7	0.100	0.447	5.15	13.7	14.6	1.47	21.9	1.07	83	0.127
	2011	Jun	19.9	3.57	23.1	0.059	0.353	3.55	6.35	7.99	0.627	17.2	1.22	35	0.115
	2011	Jul	4.16	0.770	5.40	0.014	0.079	0.683	1.16	1.86	0.146	3.88	0.296	10.3	0.030
	2011	Aug	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2011	Sep	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Total:		*301*	*87.5*	*688*	*1.88*	*5.29*	*65.5*	*161*	*205*	*25.6*	*332*	*18.0*	*1023*	*3.11*
BR	2011	Oct	17.6	7.43	57.1	0.159	0.282	1.83	15.1	17.1	1.91	19.3	2.06	79	0.332
	2011	Nov	39.8	13.5	114	0.346	0.663	4.60	25.3	38.2	3.96	54.0	6.51	158	0.594
	2011	Dec	48.9	20.2	138	0.365	1.0077	16.4	15.1	46.6	4.21	74.3	6.69	179	0.531
	2012	Jan	17.4	9.65	66.6	0.116	0.483	13.6	5.49	23.0	1.41	27.4	2.42	78	0.313
	2012	Feb	12.5	3.01	35.3	0.050	0.401	4.01	3.91	11.2	0.650	15.9	1.22	41	1.83
	2012	Mar	30.7	4.98	45.7	0.117	0.422	3.58	11.5	13.1	2.00	26.5	2.19	66	0.370
	2012	Apr	7.54	1.39	13.8	0.037	0.108	0.459	1.56	4.35	0.455	8.69	0.709	19.1	0.087
	2012	May	6.43	1.15	9.61	0.025	0.142	0.811	1.07	3.26	0.324	6.75	0.552	12.3	0.006
	2012	Jun	2.54	0.497	3.30	0.010	0.068	0.763	0.544	1.18	0.091	2.89	0.197	0.86	0.000
	2012	Jul	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2012	Aug	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2012	Sep	0.057	0.024	0.144	0.001	0.001	0.009	0.047	0.053	0.007	0.072	0.009	0.219	0.001
	2012	Oct	2.48	1.06	6.28	0.025	0.061	0.405	2.04	2.30	0.291	3.15	0.3967	9.6	0.054
	Total:		*186*	*62.9*	*489*	*1.25*	*3.64*	*46.5*	*81.7*	*160*	*15.3*	*239*	*22.9*	*645*	*4.12*

Table A.6: Continued.

Site	Year	Month	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO4-S	Zn
LU	2010	Oct	10.3	33.6	29.4	0.071	0.497	14.7	1.91	6.26	1.15	10.9	1.41	29.5	0.083
	2010	Nov	15.0	22.7	52.5	0.096	0.600	11.6	6.12	8.69	1.38	61.6	2.05	48	0.145
	2010	Dec	38.4	8.83	203	0.196	1.42	17.3	34.5	7.67	2.98	477	5.48	151	0.654
	2011	Jan	21.5	4.98	109	0.108	0.814	9.56	18.9	4.75	1.64	250	2.95	81	0.346
	2011	Feb	14.8	3.86	27.6	0.054	0.756	5.64	8.60	7.56	0.811	15.4	0.902	24.0	0.052
	2011	Mar	16.7	4.35	31.1	0.061	0.853	6.36	9.71	8.54	0.916	17.4	1.02	27.0	0.059
	2011	Apr	152	34.5	254	0.461	5.365	54.6	73.1	69.6	6.64	160	4.81	254	0.873
	2011	May	10.7	2.23	16.4	0.037	0.411	4.02	4.26	4.01	0.472	8.00	0.378	18.2	0.052
	2011	Jun	12.2	4.69	19.1	0.042	0.768	6.70	4.79	3.94	0.483	9.67	1.07	25.0	0.056
	2011	Jul	0.818	0.347	1.309	0.003	0.056	0.472	0.295	0.271	0.032	0.648	0.079	1.890	0.004
	2011	Aug	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2011	Sep	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Total:		*293*	*120*	*744*	*1.13*	*11.5*	*131*	*162*	*121*	*16.5*	*1011*	*20.1*	*661*	*2.32*
LU	2011	Oct	10.4	3.77	110	0.248	0.615	1.90	5.02	22.8	3.46	16.3	4.74	143	0.387
	2011	Nov	22.3	7.78	154	0.343	1.18	4.83	8.88	30.9	2.72	29.5	7.87	229	0.520
	2011	Dec	47.1	14.0	336	0.682	2.30	6.95	9.73	64.8	5.70	66.5	16.2	686	0.916
	2012	Jan	16.8	6.42	137	0.263	0.814	4.62	3.89	29.2	2.82	29.3	6.25	181	0.335
	2012	Feb	12.1	5.76	100	0.174	0.878	7.51	2.88	19.9	1.56	17.9	4.41	124	0.387
	2012	Mar	33.7	5.06	76.3	0.102	1.10	7.20	12.3	13.2	1.58	24.9	3.62	84	1.25
	2012	Apr	7.07	1.31	22.8	0.044	0.3143	1.26	1.18	4.38	0.415	7.23	1.06	25.0	0.022
	2012	May	1.16	0.203	3.74	0.007	0.056	0.183	0.169	0.747	0.072	1.21	0.173	4.4	0.000
	2012	Jun	0.360	0.055	1.55	0.003	0.016	0.038	0.046	0.291	0.028	0.509	0.073	3.02	0.000
	2012	Jul	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2012	Aug	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2012	Sep	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.000
	2012	Oct	8.07	3.32	67.9	0.170	0.593	1.84	3.64	14.1	1.44	9.97	4.15	87	0.345
	Total:		*159*	*47.7*	*1009*	*2.04*	*7.87*	*36.3*	*47.7*	*200*	*19.8*	*203*	*48.5*	*1566*	*4.16*

Table A.6: Continued.

Site	Year	Month	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO4-S	Zn
D4	2010	Oct	6.52	2.53	13.0	0.062	0.238	2.44	1.85	5.77	1.09	8.29	0.743	23.7	0.077
	2010	Nov	5.99	2.16	11.3	0.060	0.187	2.83	2.22	5.31	0.921	6.89	0.627	22.1	0.057
	2010	Dec	45.3	14.9	69.7	0.426	0.961	3.17	19.9	34.9	6.54	36.7	3.77	149	0.290
	2011	Jan	25.9	8.56	40.3	0.244	0.550	1.83	11.4	20.3	3.75	21.2	2.19	86	0.166
	2011	Feb	17.9	6.08	32.9	0.170	0.380	1.43	7.51	18.6	2.63	17.7	1.98	61	0.115
	2011	Mar	20.2	6.86	37.2	0.192	0.429	1.62	8.48	21.0	2.97	20.0	2.23	68	0.129
	2011	Apr	192	66.9	311	1.75	5.03	36.5	88.7	165	24.1	215	11.5	569	2.20
	2011	May	71.3	18.1	140	0.376	1.84	7.62	54.9	56.0	4.79	89.2	5.51	190	0.625
	2011	Jun	49.5	17.1	55.5	0.199	1.54	16.7	25.8	23.6	2.58	56.8	3.35	91	0.479
	2011	Jul	14.3	6.39	9.08	0.012	0.471	8.50	6.17	3.95	0.277	7.60	0.517	8.0	0.067
	2011	Aug	0.977	0.438	0.623	0.001	0.032	0.582	0.423	0.271	0.019	0.521	0.035	0.55	0.005
	2011	Sep	0.722	0.683	3.856	0.020	0.038	0.032	0.399	1.93	0.182	1.48	0.239	8.9	0.025
	Total:		*451*	*151*	*724*	*3.51*	*11.7*	*83.2*	*228*	*356*	*49.8*	*481*	*32.7*	*1277*	*4.23*
D4	2011	Oct	15.1	13.8	77.9	0.401	0.774	0.678	9.05	38.9	3.70	30.1	4.88	179	0.517
	2011	Nov	14.5	6.13	22.6	0.155	0.437	1.29	6.84	13.5	1.94	19.6	2.27	58	0.152
	2011	Dec	56.8	21.8	108	0.541	1.71	3.09	12.4	51.3	7.53	79.9	7.97	204	0.483
	2012	Jan	20.2	7.16	43.8	0.183	0.510	0.771	5.61	20.9	2.57	28.5	3.05	86	0.207
	2012	Feb	14.6	4.45	25.6	0.110	0.305	0.091	15.4	12.6	1.65	18.5	1.90	57	0.142
	2012	Mar	30.8	8.16	44.1	0.235	0.842	0.960	8.45	18.8	3.20	30.2	3.70	95	0.237
	2012	Apr	5.29	1.42	8.71	0.045	0.158	0.118	1.23	3.94	0.515	6.39	0.683	18.5	0.053
	2012	May	1.80	0.422	2.78	0.016	0.054	0.047	0.381	1.37	0.169	2.35	0.214	6.6	0.005
	2012	Jun	2.07	0.410	3.03	0.017	0.067	0.077	0.204	1.44	0.145	2.67	0.267	8.0	0.000
	2012	Jul	0.004	0.001	0.006	0.000	0.000	0.000	0.000	0.003	0.000	0.006	0.001	0.017	0.000
	2012	Aug	0.253	0.085	0.376	0.003	0.009	0.018	0.094	0.192	0.034	0.306	0.032	0.957	0.003
	2012	Sep	3.71	1.43	5.53	0.044	0.129	0.304	1.74	2.90	0.579	4.38	0.466	13.9	0.056
	2012	Oct	14.2	5.49	21.2	0.170	0.495	1.16	6.66	11.1	2.22	16.8	1.79	53	0.214
	Total:		*179*	*70.8*	*363*	*1.92*	*5.49*	*8.60*	*68.0*	*177*	*24.2*	*240*	*27.2*	*778*	*2.07*

Table A.6: Continued.

Site	Year	Month	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO4-S	Zn
D5	2010	Oct	49.1	3.68	136	0.023	0.688	28.0	19.3	62.2	0.722	61.5	2.36	141	0.141
	2010	Nov	49.5	5.50	135	0.082	0.702	24.6	25.6	63.1	1.79	61.0	2.82	151	0.290
	2010	Dec	44.7	9.39	110	0.125	0.711	34.4	31.3	49.7	2.47	48.8	3.68	159	0.545
	2011	Jan	23.7	5.05	58.8	0.065	0.371	17.7	16.6	26.8	1.27	26.1	1.96	85	0.281
	2011	Feb	16.4	4.42	50.1	0.024	0.166	4.10	10.7	24.7	0.320	21.6	1.42	66	0.082
	2011	Mar	18.5	4.99	56.6	0.027	0.187	4.62	12.0	27.9	0.361	24.4	1.61	74	0.092
	2011	Apr	112	31.3	387	0.238	2.18	52.8	85.8	131	2.98	190	3.98	381	1.84
	2011	May	27.2	5.17	89.1	0.039	0.469	8.48	19.7	32.2	0.516	40.8	1.83	91	0.303
	2011	Jun	7.99	1.06	11.1	0.026	0.162	0.804	2.23	3.87	0.281	9.52	0.686	24.0	0.052
	2011	Jul	0.686	0.085	0.439	0.002	0.013	0.082	0.154	0.194	0.029	0.638	0.045	2.03	0.004
	2011	Aug	0.013	0.001	0.008	0.000	0.000	0.004	0.005	0.003	0.000	0.010	0.000	0.029	0.000
	2011	Sep	0.013	0.001	0.060	0.000	0.000	0.008	0.012	0.028	0.002	0.027	0.001	0.091	0.000
	Total:		*350*	*70.6*	*1034*	*0.651*	*5.65*	*176*	*223*	*422*	*10.8*	*484*	*20.4*	*1173*	*3.63*
D5	2011	Oct	8.13	0.780	46.9	0.001	0.061	1.34	8.36	22.6	0.517	18.4	1.78	57	0.119
	2011	Nov	39.9	4.71	321	0.043	0.523	3.44	19.5	48.3	0.583	66.4	5.47	161	0.534
	2011	Dec	52.0	10.2	196	0.081	0.744	8.54	23.1	66.4	0.798	96.1	7.19	207	1.47
	2012	Jan	18.5	7.40	63.4	0.003	0.363	9.58	7.05	26.4	0.410	34.8	2.69	84	0.092
	2012	Feb	13.3	5.97	40.6	0.026	0.394	30.3	7.88	16.7	0.695	22.4	2.06	59	0.185
	2012	Mar	58.4	7.51	124	0.005	1.08	5.22	27.0	48.0	1.16	74.0	6.99	174	0.393
	2012	Apr	28.2	1.70	79.9	0.001	0.320	1.12	11.6	31.4	0.222	46.9	3.48	106	0.151
	2012	May	13.8	0.968	37.4	0.008	0.208	1.23	4.47	15.4	0.163	26.6	1.49	50	0.016
	2012	Jun	2.23	0.128	6.11	0.004	0.033	0.377	0.192	2.44	0.043	3.73	0.264	5.0	0.000
	2012	Jul	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2012	Aug	0.012	0.001	0.039	0.000	0.000	0.007	0.003	0.016	0.004	0.046	0.001	0.009	0.000
	2012	Sep	0.002	0.000	0.005	0.000	0.000	0.000	0.002	0.002	0.000	0.003	0.000	0.008	0.000
	2012	Oct	6.57	1.21	16.3	0.000	0.130	1.04	7.31	7.51	0.365	9.63	0.961	25.5	0.098
	Total:		*241*	*40.6*	*932*	*0.172*	*3.85*	*62.2*	*116*	*285*	*4.96*	*399*	*32.4*	*929*	*3.06*

Table A.7: Catchment-weighted (mg/m2) deposition input fluxes of metals, cations, and sulphate to the six catchments for both budget years. Table continued on the next 5 pages.

Site	Date	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
C1	2010-10-18	24.7	1.92	30.3	0.126	5.72	1.26	6.85	14.6	0.404	19.0	1.49	232	0.476
	2010-11-01	24.7	1.13	10.2	0.011	0.238	0.320	4.86	1.90	0.096	7.32	0.079	11.6	0.133
	2010-11-15	11.0	0.877	8.77	0.033	1.02	2.08	4.38	1.75	0.110	8.55	0.035	10.8	0.191
	2010-11-29	47.4	3.32	13.3	0.033	0.658	3.32	13.3	3.32	0.109	10.4	0.046	18.7	0.262
	2011-01-05	49.0	4.51	59.2	0.070	6.82	5.49	23.1	9.71	0.288	375	1.50	49	3.09
	2011-02-03	12.2	1.06	4.17	0.045	2.58	1.62	1.90	0.731	0.038	8.05	0.862	6.3	0.127
	2011-03-09	20.5	8.48	20.7	0.074	2.84	21.6	9.20	6.87	0.181	17.6	1.41	17.9	0.609
	2011-03-30	22.4	2.47	16.4	0.044	0.184	2.91	8.07	18.2	0.095	8.96	0.068	27.1	0.112
	2011-04-12	18.1	3.01	23.2	0.001	0.210	2.45	10.7	4.78	0.188	12.4	0.106	18.9	0.373
	2011-04-29	127	15.4	56.5	0.006	1.27	12.1	439	46.2	0.278	76.4	0.334	89	2.53
	2011-06-01	28.1	0.365	12.2	0.001	0.466	0.843	23.1	5.53	0.202	11.2	2.77	18.2	0.477
	2011-06-30	103	0.207	7.55	0.023	0.247	0.827	43.5	1.03	0.124	6.00	0.069	52	0.365
	2011-08-05	54.3	0.358	10.5	0.004	0.036	1.35	25.0	1.72	0.120	13.6	0.239	14.1	0.328
	2011-09-06	38.0	1.50	22.5	0.002	0.436	0.717	9.95	3.34	0.258	13.0	0.301	21.1	0.358
	2011-10-05	41.7	1.61	11.1	0.002	0.367	1.00	19.6	4.25	0.048	12.8	0.164	26.1	0.257
	Total:	*623*	*46.2*	*307*	*0.477*	*23.1*	*57.9*	*642*	*124*	*2.54*	*600*	*9.47*	*614*	*9.68*
C1	2011-10-21	42.2	1.55	9.52	0.002	0.205	1.34	8.81	2.25	0.124	9.15	0.164	13.0	0.313
	2011-11-04	33.8	1.78	17.4	0.005	0.285	0.804	2.26	2.39	0.131	11.9	0.164	25.2	0.279
	2011-11-18	30.4	0.231	9.15	0.002	0.512	1.25	5.38	1.29	0.062	3.68	0.769	14.3	0.002
	2011-11-30	25.7	0.808	14.0	0.037	0.598	2.86	9.47	6.43	0.630	10.1	0.397	23.8	0.524
	2012-01-12	59.2	1.31	16.5	0.003	1.81	3.46	27.6	2.02	0.111	16.6	0.458	21.8	0.189
	2012-02-17	45.0	0.007	22.8	0.002	0.972	0.815	7.16	0.305	0.231	15.0	0.515	26.9	0.344
	2012-03-18	43.4	0.007	26.1	0.010	0.659	0.586	10.9	3.38	1.51	13.2	0.435	23.1	1.003
	2012-04-13	20.8	0.003	18.1	0.008	0.482	0.208	10.3	2.40	0.210	12.6	0.274	26.9	0.502
	2012-04-27	39.6	0.006	12.9	0.002	0.750	0.396	12.2	1.40	0.111	8.55	0.336	23.4	0.221
	2012-06-06	43.2	1.39	28.1	0.076	0.801	3.90	7.23	7.44	0.552	12.9	0.796	51	0.002
	2012-07-03	37.4	5.60	15.8	0.002	0.329	2.98	13.0	3.37	0.115	10.9	0.357	13.1	0.315
	2012-08-01	35.4	0.487	56.9	0.002	0.991	2.66	21.6	12.1	0.081	113	0.680	20.8	0.660
	2012-08-29	41.1	0.986	19.3	0.002	0.654	1.97	43.1	3.95	0.378	33.7	0.247	23.1	0.813
	2012-10-15	103	1.74	24.4	0.005	1.03	3.80	44.4	12.7	0.000	12.5	0.431	42	0.968
	Total:	*600*	*15.9*	*291*	*0.158*	*10.1*	*27.0*	*223*	*61.3*	*4.25*	*284*	*6.02*	*349*	*6.14*

Site	Date	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
C2	2010-10-18	24.7	3.06	85.5	0.422	6.90	4.14	17.4	3.23	0.404	22.6	3.03	129	0.853
	2010-11-01	24.7	1.18	10.3	0.017	0.288	0.592	4.39	1.95	0.096	8.60	0.121	10.8	0.119
	2010-11-15	10.6	1.27	8.44	0.035	1.07	20.8	3.59	1.58	0.122	4.22	0.036	8.4	0.160
	2010-11-29	47.4	7.58	48.8	0.071	1.76	8.06	22.3	8.53	0.531	22.3	0.090	75	1.39
	2011-01-05	44.7	4.56	13.7	0.091	2.72	6.97	7.95	2.72	4.36	12.3	1.26	25.3	0.371
	2011-02-03	13.3	1.04	4.17	0.061	3.05	1.16	1.98	0.692	0.034	7.86	0.938	9.1	0.086
	2011-03-09	16.9	12.2	18.2	0.089	1.72	35.6	9.95	8.40	0.247	16.2	1.27	12.9	0.519
	2011-03-30	26.0	4.68	47.3	0.184	0.213	29.1	24.7	51.7	0.275	26.2	0.150	38	0.607
	2011-04-12	16.4	7.74	25.3	0.001	0.568	8.82	7.01	6.01	0.181	14.6	0.108	17.9	0.302
	2011-04-29	127	15.4	56.5	0.006	1.27	12.1	439	46.2	0.278	76.4	0.334	49	2.53
	2011-06-01	26.4	0.471	11.3	0.007	0.144	0.870	10.3	2.11	0.162	7.17	0.098	10.6	0.145
	2011-06-30	103	0.414	14.1	0.034	0.232	1.03	41.4	2.17	0.391	9.51	0.217	43	0.634
	2011-08-05	54.3	0.367	14.8	0.032	0.023	1.85	29.4	1.77	0.103	18.9	0.267	14.7	0.338
	2011-09-06	39.8	1.63	22.7	0.002	0.576	1.93	13.6	4.65	0.262	20.0	0.368	24.4	0.370
	2011-10-05	41.1	1.58	13.8	0.002	0.253	1.51	9.58	3.13	0.171	12.3	0.255	23.0	0.233
	Total:	*617*	*63.2*	*395*	*1.05*	*20.8*	*134*	*642*	*145*	*7.62*	*279*	*8.55*	*490*	*8.65*
C2	2011-10-21	37.7	1.39	6.00	0.002	0.077	0.773	6.06	1.38	0.048	7.47	0.064	10.6	0.084
	2011-11-04	29.3	1.54	15.9	0.001	0.284	0.529	36.2	1.86	0.105	9.40	0.156	22.5	0.233
	2011-11-18	38.3	0.180	11.7	0.002	0.386	1.17	6.11	1.77	0.103	9.65	0.228	17.3	0.002
	2011-11-30	24.0	1.83	12.5	0.045	0.597	4.41	4.89	2.91	0.128	8.39	0.527	21.2	0.294
	2012-01-12	69.2	2.68	21.6	0.003	2.24	3.21	17.5	3.01	0.220	15.8	0.751	32.4	0.003
	2012-02-17	28.3	1.46	6.14	0.001	0.573	2.70	8.24	0.272	0.083	5.15	0.340	3.7	0.060
	2012-03-18	37.7	0.006	26.2	0.002	0.864	0.252	10.0	2.60	0.214	16.9	0.551	25.1	1.15
	2012-04-13	21.4	0.003	17.9	0.021	0.370	0.214	3.35	1.95	0.150	9.12	0.313	24.3	0.411
	2012-04-27	39.3	0.379	12.6	0.002	0.809	1.15	4.07	0.383	0.107	7.30	0.424	16.3	0.177
	2012-05-24	7.15	0.100	20.2	0.027	0.198	0.271	3.55	3.05	0.236	4.34	0.274	4.4	0.076
	2012-06-06	41.1	0.006	12.1	0.082	0.273	0.411	3.62	2.84	0.176	3.28	0.105	112	0.002
	2012-07-03	36.7	0.006	16.6	0.002	0.324	2.53	15.4	3.30	0.000	4.45	0.230	21.6	0.370
	2012-08-01	40.9	0.028	48.9	0.002	1.03	2.90	30.9	10.8	0.143	91.4	0.566	24.8	1.23
	2012-08-29	42.2	0.591	16.3	0.002	0.336	1.69	1.50	3.12	0.485	2.66	0.282	26.2	0.420
	2012-10-15	103	1.64	17.7	0.005	0.002	2.77	9.51	5.39	0.000	4.92	0.463	27.8	0.765
	Total:	*596*	*11.8*	*263*	*0.200*	*8.37*	*25.0*	*161*	*44.7*	*2.20*	*200*	*5.27*	*391*	*5.28*

Table A.7: Continued.

Site	Date	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
BR	2010-11-01	49.3	2.32	19.8	0.022	0.418	0.592	9.37	3.55	0.177	14.0	0.240	17.6	0.315
	2010-11-15	11.2	0.896	7.17	0.017	0.418	4.26	4.71	1.34	0.539	3.70	0.014	9.2	0.461
	2010-11-29	47.4	3.32	17.1	0.066	2.03	3.79	19.0	3.79	0.166	14.7	0.080	26.9	0.392
	2011-01-05	56.8	3.69	10.1	0.048	2.48	2.33	10.5	2.10	0.123	15.3	1.13	17.3	0.614
	2011-02-03	21.9	1.40	2.85	0.016	0.831	1.05	3.44	0.899	0.024	14.1	0.292	7.9	0.103
	2011-03-09	22.2	4.23	14.1	0.026	1.47	6.51	8.57	4.51	0.076	15.2	0.703	12.2	0.526
	2011-03-30	17.1	2.39	27.6	0.025	0.781	22.5	6.82	20.6	0.163	9.21	0.032	21.6	0.205
	2011-04-12	20.1	3.14	25.0	0.001	0.349	4.00	9.11	6.53	0.187	19.1	0.153	20.0	0.423
	2011-04-29	127	3.43	30.3	0.006	1.23	14.6	40.1	4.83	0.308	11.5	7.66	59	0.350
	2011-06-01	25.4	3.57	10.1	0.001	0.151	11.5	20.6	2.49	0.231	6.01	0.277	12.0	0.061
	2011-06-30	103	7.03	20.9	0.154	0.189	3.41	31.3	11.8	1.86	31.2	1.75	262	0.179
	2011-09-06	96.9	3.84	30.3	0.005	0.302	1.78	29.0	7.82	0.627	26.6	0.576	78	0.725
	2011-10-05	39.0	27.8	649	0.002	1.43	26.0	11.2	159	0.045	28.9	0.154	29.2	0.240
	Total:	*638*	*67.1*	*864*	*0.390*	*12.1*	*102*	*204*	*229*	*4.52*	*210*	*13.0*	*573*	*4.60*
BR	2011-10-21	41.9	1.93	11.8	0.002	0.137	2.01	9.86	2.39	0.138	11.3	0.209	15.8	0.127
	2011-11-04	29.2	1.55	14.1	0.001	0.273	0.646	2.34	1.95	0.106	8.18	0.066	15.9	0.363
	2011-11-18	36.4	0.646	13.6	0.002	0.390	3.07	4.52	1.95	0.151	4.71	0.314	23.9	0.002
	2011-11-30	25.2	1.24	12.5	0.032	0.628	2.82	6.20	2.66	0.116	9.53	0.291	24.2	0.337
	2012-01-12	65.4	0.914	21.4	0.003	2.45	1.43	31.3	3.35	0.148	38.1	0.715	22.5	1.286
	2012-02-17	39.8	0.006	12.0	0.002	1.61	0.398	7.14	1.39	0.115	10.1	0.008	6.5	2.060
	2012-03-18	50.3	0.058	25.3	0.003	2.81	1.07	7.31	1.44	0.211	12.7	0.222	24.6	0.356
	2012-04-15	14.0	0.298	12.3	0.003	0.123	0.468	3.16	1.36	0.130	8.25	0.086	17.3	0.334
	2012-04-27	13.3	0.084	7.21	0.013	0.482	0.533	3.23	0.797	0.071	6.48	0.234	8.4	0.192
	2012-05-24	8.12	0.158	18.0	0.007	0.172	0.360	4.96	3.18	0.031	3.05	0.062	5.1	0.000
	2012-06-06	35.9	0.336	34.5	0.029	0.557	1.96	23.4	7.88	0.426	27.9	0.183	57	0.002
	2012-07-03	35.4	0.005	14.2	0.002	0.334	2.81	12.5	3.35	0.163	6.36	0.527	21.3	0.568
	2012-08-01	37.7	2.87	47.2	0.002	2.72	3.03	13.8	5.35	0.151	32.3	0.886	30.9	0.910
	2012-08-29	38.4	0.807	15.1	0.002	0.491	1.23	4.03	2.77	0.000	3.34	0.153	26.2	0.175
	2012-10-15	103	1.44	21.8	0.005	0.002	2.36	3.44	6.74	0.000	6.05	0.252	32.6	0.513
	Total:	*574*	*12.3*	*281*	*0.109*	*13.2*	*24.2*	*137*	*46.6*	*1.96*	*188*	*4.21*	*332*	*7.22*

Table A.7: Continued.

Site	Date	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
LU	2010-10-18	24.7	1.77	38.2	0.189	4.34	1.36	5.25	28.5	20.9	9.66	1.74	27.6	0.555
	2010-11-01	24.7	1.55	12.9	0.031	1.13	1.11	4.51	2.51	0.145	10.3	0.320	15.1	0.207
	2010-11-15	9.50	0.950	8.46	0.017	0.49	1.24	3.71	1.62	0.113	5.89	0.019	7.5	0.190
	2010-11-29	47.4	8.06	51.7	0.069	2.87	9.96	28.9	46.5	0.513	34.6	0.130	75	1.26
	2011-01-05	39.1	10.5	113	0.220	1.41	28.5	7.87	26.1	2.50	38.0	5.91	53	0.232
	2011-02-03	11.5	0.842	2.21	0.025	2.58	1.40	2.11	0.611	0.024	13.7	0.439	5.9	0.091
	2011-03-09	14.5	6.67	21.9	0.041	2.03	7.20	9.37	5.37	0.271	31.4	0.653	19.3	0.750
	2011-03-30	10.1	1.21	12.5	0.009	0.741	5.64	5.34	2.01	0.089	8.16	0.022	12.1	0.144
	2011-04-12	14.9	2.95	27.7	0.018	0.528	2.80	11.1	5.45	0.225	18.9	0.205	19.1	1.74
	2011-04-29	127	3.18	38.7	0.057	1.75	7.50	55.1	5.85	0.281	22.3	8.93	52	0.909
	2011-06-01	23.1	0.226	6.56	0.001	0.108	0.692	7.14	1.48	0.068	2.78	0.045	9.1	0.067
	2011-06-30	103	11.8	11.5	0.028	0.002	2.33	57.3	2.77	0.295	18.4	0.735	37	2.03
	2011-08-04	54.3	2.75	27.2	0.048	1.02	2.05	108	10.8	0.129	33.5	0.727	71	0.475
	2011-09-06	33.9	1.71	28.7	0.049	0.499	0.685	6.32	4.88	0.101	19.5	0.581	37	0.976
	2011-10-05	37.7	12.6	528	0.275	0.684	34.9	32.6	100	3.01	82.5	4.46	28.5	0.677
	Total:	*576*	*66.7*	*930*	*1.08*	*20.2*	*107*	*345*	*245*	*28.6*	*350*	*24.9*	*470*	*10.3*
LU	2011-10-19	39.5	2.40	16.3	0.002	0.529	1.32	6.63	3.79	0.078	16.7	0.209	20.4	0.219
	2011-11-04	38.7	1.94	11.1	0.002	0.526	0.778	19.4	1.17	0.071	4.03	0.142	18.2	0.202
	2011-11-18	27.4	0.454	8.17	0.001	0.684	1.79	4.08	1.34	0.086	2.61	0.294	13.6	0.001
	2011-11-30	27.9	1.70	32.0	0.086	1.27	4.11	14.2	9.72	0.304	40.7	0.652	218	1.21
	2012-01-13	52.3	2.41	48.8	0.079	6.18	3.98	11.2	7.65	0.451	77.7	1.73	109	2.73
	2012-02-17	37.0	0.006	24.7	0.002	0.636	0.800	12.6	1.23	0.208	23.1	0.257	18.1	0.325
	2012-03-18	48.7	0.208	39.4	0.002	1.44	0.958	8.11	3.77	0.353	35.1	0.647	36	1.73
	2012-04-15	15.6	0.019	14.8	0.001	0.124	0.010	2.98	1.37	0.115	6.69	0.114	16.4	0.154
	2012-04-26	29.6	0.322	12.7	0.018	0.563	0.949	1.88	2.81	0.105	8.03	0.157	13.4	0.001
	2012-06-05	42.4	0.408	18.1	0.039	0.530	1.14	5.95	3.72	0.233	7.71	0.076	212	0.002
	2012-07-03	38.4	0.342	29.6	0.002	0.881	2.82	6.61	4.20	0.199	5.67	0.794	31.4	0.551
	2012-08-01	27.8	1.44	55.7	0.001	1.98	2.53	70.1	17.8	0.336	93.8	1.09	38	1.24
	2012-08-29	28.6	0.543	14.7	0.001	0.302	0.915	25.0	5.54	0.000	5.00	0.209	27.9	0.163
	2012-10-15	103	1.03	14.0	0.005	0.002	2.26	2.54	4.39	0.000	7.08	0.343	32.9	0.635
	Total:	*556*	*13.2*	*340*	*0.242*	*15.7*	*24.3*	*191*	*68.6*	*2.54*	*334*	*6.71*	*806*	*9.17*

Table A.7: Continued.

Site	Date	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
D4	2010-10-18	24.7	1.63	22.9	0.047	3.62	0.961	5.35	26.2	0.569	7.20	0.747	111	0.345
	2010-11-01	24.7	1.33	19.9	0.025	0.350	0.789	7.59	3.55	0.176	23.3	0.153	17.7	2.17
	2010-11-15	8.61	0.947	7.23	0.008	0.161	1.03	3.44	1.38	0.060	6.54	0.008	7.6	0.244
	2010-12-01	47.4	2.37	11.4	0.028	0.237	0.948	13.3	2.84	0.085	10.9	0.026	13.5	0.303
	2011-01-05	30.0	3.58	21.5	0.031	1.32	3.09	14.6	3.30	0.273	41.6	0.559	29.7	1.71
	2011-02-03	21.5	2.28	4.28	0.023	1.08	0.990	3.40	0.990	0.037	21.9	0.413	8.9	0.222
	2011-03-10	40.8	6.41	41.4	0.002	1.70	6.34	20.2	10.2	0.527	48.6	0.608	29.5	3.05
	2011-03-30	15.3	3.51	26.9	0.017	0.467	13.0	7.17	17.4	0.135	14.2	0.029	15.4	0.561
	2011-04-12	17.7	5.00	33.2	0.033	0.354	5.52	11.5	6.90	0.255	22.4	0.162	19.1	1.05
	2011-04-29	127	1.78	35.5	0.006	1.36	9.41	42.5	5.85	0.307	26.7	12.7	57	0.645
	2011-06-01	23.1	1.77	11.0	0.001	0.178	1.95	21.7	2.00	0.225	4.86	0.217	23.3	0.243
	2011-06-30	103	12.8	67.5	0.484	2.61	11.9	110	29.4	5.06	103	8.44	26.5	0.699
	2011-08-04	54.3	0.008	14.9	0.014	0.001	0.543	21.5	1.90	0.000	6.05	0.014	17.0	0.129
	2011-09-07	21.9	1.90	14.5	0.001	0.901	1.51	6.29	2.90	0.319	6.39	0.302	20.3	1.37
	2011-10-06	19.8	10.4	46.6	0.344	0.932	1.11	21.3	26.1	3.54	31.3	4.24	16.5	0.765
	Total:	*580*	*55.7*	*379*	*1.06*	*15.3*	*59.1*	*310*	*141*	*11.6*	*374*	*28.6*	*413*	*13.5*
D4	2011-10-19	39.5	1.35	12.4	0.002	0.327	0.999	6.95	2.17	0.102	11.0	0.115	4.1	0.203
	2011-11-02	40.6	2.16	8.40	0.002	0.305	0.850	47.4	1.21	0.112	10.4	0.036	14.5	0.142
	2011-11-16	41.7	1.71	15.7	0.002	1.18	2.38	6.42	2.23	0.152	11.3	0.202	22.6	0.002
	2011-11-30	26.8	0.972	24.8	0.036	0.662	1.42	4.67	3.94	0.176	13.9	0.362	35	0.104
	2012-01-12	62.1	1.63	16.6	0.003	0.737	2.26	16.4	1.69	0.118	10.6	0.244	21.2	0.003
	2012-02-16	36.5	0.005	24.3	0.002	0.627	0.789	12.4	1.21	0.205	22.8	0.253	17.9	0.321
	2012-03-18	49.9	0.007	23.4	0.002	0.720	0.499	19.1	1.18	0.232	22.2	0.195	24.4	0.641
	2012-04-15	16.2	0.214	19.0	0.015	0.153	0.507	3.33	1.74	0.128	10.5	0.142	17.5	0.256
	2012-04-26	38.8	5.82	10.2	0.008	0.270	0.756	3.28	0.114	0.090	2.74	0.123	17.3	0.002
	2012-06-05	42.5	0.006	12.9	0.040	0.266	0.285	3.31	2.79	0.205	2.79	0.108	129	0.002
	2012-07-04	41.3	0.276	25.2	0.002	0.659	3.78	23.4	4.11	0.294	11.4	0.395	37	0.674
	2012-08-02	40.1	1.63	59.1	0.002	1.03	3.56	10.4	11.9	0.191	111	0.513	38	1.07
	2012-08-29	28.6	0.286	3.90	0.001	0.001	0.629	0.709	1.22	0.000	1.97	0.096	9.2	0.177
	2012-10-15	103	1.03	14.0	0.005	0.002	2.26	2.54	4.39	0.000	7.08	0.343	32.9	0.635
	Total:	*607*	*17.1*	*270*	*0.124*	*6.94*	*21.0*	*160*	*39.9*	*2.01*	*249*	*3.13*	*421*	*4.75*

Table A.7: Continued.

Site	Date	Flow (mm)	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4-S	Zn
D5	2010-10-18	24.7	1.58	20.0	0.048	1.92	0.542	5.45	7.40	0.360	5.60	0.671	22.9	0.224
	2010-11-01	24.7	2.14	16.5	0.029	0.471	5.00	6.51	3.18	0.212	25.9	0.164	13.2	0.220
	2010-11-15	8.93	0.804	6.97	0.013	0.329	8.75	2.86	1.43	0.071	3.66	0.009	6.7	0.113
	2010-12-01	47.4	2.84	9.01	0.024	0.237	1.42	12.8	2.84	0.066	10.9	0.024	13.5	0.223
	2011-01-05	30.0	5.47	45.8	0.075	2.27	3.52	22.1	5.80	0.409	140	0.910	66	3.52
	2011-02-03	21.5	1.79	4.48	0.029	0.904	1.12	3.55	1.16	0.061	25.7	0.426	8.3	0.188
	2011-03-10	40.8	9.23	332	0.011	1.45	7.97	39.3	23.9	0.767	71.0	0.397	45	1.50
	2011-03-30	16.1	10.3	212	0.008	0.200	14.0	6.91	40.7	0.723	9.65	0.004	13.6	0.087
	2011-04-12	17.1	4.52	25.3	0.001	0.393	4.51	11.3	4.79	0.213	12.5	0.166	17.1	0.982
	2011-04-29	127	5.09	45.9	0.006	1.32	7.89	135	6.11	0.498	28.3	12.9	47	4.53
	2011-06-01	23.1	1.77	11.0	0.001	0.178	1.95	21.7	2.00	0.225	4.86	0.217	23.3	0.243
	2011-06-30	103	12.8	67.5	0.484	2.61	11.9	110	29.4	5.06	103	8.44	26.5	0.699
	2011-08-04	54.3	0.008	14.9	0.014	0.001	0.543	21.5	1.90	0.000	6.05	0.014	17.0	0.129
	2011-09-07	21.9	1.90	14.5	0.001	0.901	1.51	6.29	2.90	0.319	6.39	0.302	20.3	1.37
	2011-10-06	19.8	1.54	9.46	0.001	0.243	2.45	5.26	2.51	0.193	6.52	0.162	15.7	0.487
	Total:	*581*	*61.8*	*835*	*0.744*	*13.4*	*73.1*	*410*	*136*	*9.17*	*460*	*24.8*	*356*	*14.5*
D5	2011-10-19	39.5	2.38	12.5	0.002	0.343	2.49	29.9	3.46	0.164	16.8	0.110	13.3	0.874
	2011-11-02	40.9	3.08	7.75	0.002	0.345	2.18	0.819	1.51	0.083	11.5	0.113	18.2	0.862
	2011-11-16	39.8	0.864	110	0.002	0.334	1.71	5.51	1.60	0.106	8.39	0.125	18.1	0.002
	2011-11-30	26.8	1.58	5.04	0.001	0.350	2.71	3.80	0.876	0.079	1.22	0.175	110	0.397
	2012-01-12	62.1	1.24	15.0	0.003	0.482	3.65	54.4	3.23	0.195	20.7	0.417	20.1	0.003
	2012-02-16	37.0	0.006	13.7	0.002	0.353	1.15	7.24	1.30	0.082	12.5	0.176	7.5	0.022
	2012-03-18	49.9	1.93	22.3	0.002	0.751	4.71	15.4	2.62	0.270	15.7	0.442	22.8	3.18
	2012-04-15	16.1	0.024	15.9	0.001	0.146	0.161	5.07	1.92	0.135	12.1	0.162	18.1	0.327
	2012-04-26	33.3	0.005	9.12	0.002	0.269	0.441	4.10	0.360	0.097	7.04	0.104	13.7	0.044
	2012-06-05	42.4	0.006	20.3	0.026	0.312	0.290	9.06	4.00	0.369	10.2	0.040	144	0.002
	2012-07-04	41.3	0.006	34.8	0.002	1.14	3.32	92.0	5.91	1.16	36.5	0.850	82	6.55
	2012-08-02	40.1	1.00	60.3	0.002	1.31	3.22	13.8	11.6	0.453	89.7	0.801	51	1.10
	2012-08-29	28.6	1.46	19.0	0.001	0.439	3.23	40.3	3.71	0.453	3.54	0.658	44	0.447
	2012-10-15	103	1.03	14.0	0.005	0.002	2.26	2.54	4.39	0.000	7.08	0.343	32.9	0.635
	Total:	*600*	*14.6*	*360*	*0.054*	*6.58*	*31.5*	*284*	*46.4*	*3.65*	*253*	*4.52*	*596*	*14.4*

Table A.8: Annual catchment-weighted (mg/m^2) input and outflow fluxes, and mass balances for metals, cations, and sulphate in the six catchments for both budget years. Table continued on next page.

Site	Budget Year	Flux	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4	Zn
C1	*2010 – 2011*	Input	46.2	307	0.477	23.1	57.9	642	124	2.54	600	9.47	1839	9.68
		Outflow	93.9	650	1.39	6.81	150	170	231	23.6	391	20.8	3408	3.13
		mass balance	-47.7	-343	-0.92	16.3	-91.7	472	-107	-21.0	210	-11.3	-1568	6.55
	2011 – 2012	Input	15.9	291	0.158	10.1	27.0	223	61.3	4.25	284	6.02	1045	6.14
		Outflow	50.2	729	1.52	5.23	46.1	137	263	21.5	388	33.3	2985	4.16
		mass balance	-34.3	-437	-1.36	4.85	-19.1	86.2	-202	-17.3	-104	-27.3	-1941	1.98
C2	*2010 – 2011*	Input	63.2	395	1.05	20.8	134	642	145	7.62	279	8.55	1469	8.65
		Outflow	88.4	2955	1.07	6.44	114	316	420	13.2	2910	13.4	3651	6.06
		mass balance	-25.2	-2560	-0.015	14.3	20.8	326	-275	-5.54	-2631	-4.82	-2182	2.60
	2011 – 2012	Input	11.8	263	0.200	8.37	25.0	161	44.7	2.20	200	5.27	1171	5.28
		Outflow	64.3	2415	0.802	6.20	86.2	235	360	7.25	2029	19.1	2656	8.19
		mass balance	-52.4	-2153	-0.601	2.17	-61.2	-73.7	-315	-5.05	-1829	-13.8	-1486	-2.90
BR	*2010 – 2011*	Input	67.1	864	0.390	12.1	102	204	229	4.52	210	13.0	1715	4.60
		Outflow	87.5	688	1.88	5.29	65.5	161	205	25.6	332	18.0	3065	3.11
		mass balance	-20.4	175	-1.49	6.79	36.9	43.2	24.2	-21.1	-122	-4.90	-1350	1.49
	2011 – 2012	Input	12.3	281	0.109	13.2	24.2	137	46.6	1.96	188	4.21	994	7.22
		Outflow	62.9	489	1.25	3.64	46.5	81.7	160	15.3	239	22.9	1932	4.12
		mass balance	-50.6	-208	-1.14	9.53	-22.3	55.5	-114	-13.3	-50.6	-18.7	-938	3.11

Table A.8: Continued.

Site	Budget Year	Flux	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	SO_4	Zn
LU	*2010 – 2011*	Input	66.7	930	1.08	20.2	107	345	245	28.6	350	24.9	1408	10.3
		Outflow	120	744	1.13	11.5	131	162	121	16.5	1011	20.1	1979	2.32
		mass balance	-53.4	186	-0.052	8.63	-23.5	183	123	12.1	-661	4.77	-571	7.97
	2011 – 2012	Input	13.2	340	0.242	15.7	24.3	191	68.6	2.54	334	6.71	2415	9.17
		Outflow	47.7	1009	2.04	7.87	36.3	47.7	200	19.8	203	48.5	4691	4.16
		mass balance	-34.5	-670	-1.79	7.78	-12.0	143	-132	-17.2	131	-41.8	-2275	5.01
D4	*2010 – 2011*	Input	55.7	379	1.06	15.3	59.1	310	141	11.6	374	28.6	1238	13.5
		Outflow	151	724	3.51	11.7	83.2	228	356	49.8	481	32.7	3825	4.23
		mass balance	-95.0	-345	-2.44	3.58	-24.2	82.3	-215	-38.3	-107	-4.17	-2587	9.28
	2011 – 2012	Input	17.1	270	0.124	6.94	21.0	160	39.9	2.01	249	3.13	1260	4.75
		Outflow	70.8	363	1.92	5.49	8.60	68.0	177	24.2	240	27.2	2331	2.07
		mass balance	-53.7	-93.2	-1.80	1.45	12.4	92.3	-137	-22.2	9.80	-24.1	-1071	2.68
D5	*2010 – 2011*	Input	61.8	835	0.744	13.4	73.1	410	136	9.17	460	24.8	1066	14.5
		Outflow	70.6	1034	0.651	5.65	176	223	422	10.8	484	20.4	3516	3.63
		mass balance	-8.85	-198	0.093	7.77	-103	187	-286	-1.58	-24.7	4.46	-2450	10.9
	2011 – 2012	Input	14.6	360	0.054	6.58	31.5	284	46.4	3.65	253	4.52	1785	14.4
		Outflow	40.6	932	0.172	3.85	62.2	116	285	4.96	399	32.4	2784	3.06
		mass balance	-26.0	-572	-0.119	2.73	-30.7	168	-239	-1.31	-146	-27.9	-1000	11.4

A5. In-house R Script for DOM Correction

```
# This is an IN-HOUSE script for use by members of Dr. Gunn's lab only. Any use outside of this lab
# should receive permission and make acknowledgement to the original author of this script. Written
# by Erik Szkokan-Emilson (final version February 2014).

# Note: this script is written to handle CSV output files from the Cary Eclipse and the Cary 60
# machines in Dr. Gunn's lab, as per the instruction files: "Gunn Cary60 Instructions.docx" and
# "Gunn CaryEclipse Instructions.docx" in the master data directory.

# Enter the name of the project folder containing uncorrected EEMs. Note: The script will read from
# any scan date subfolders that you may or may not have in your project folder.
project <- "projectnamehere"

# preserve subfolders in Corrected EEMs folder? TRUE or FALSE
presub <- TRUE

# Specify range for excitation and emission and the step values to match that of the raw files (nm)
maxEM   <- 600 #maximum emission
minEM   <- 300 #minimum emission
stepEM  <- 2   #emission step value
maxEX   <- 450 #maximum excitation
minEX   <- 220 #minimum excitation
stepEX  <- 5   #excitation step value
minAB   <- 220 #minimum absorbance
maxAB   <- 600 #maximum absorbance
stepAB  <- 1   #absorbance step value
numEM   <- ((maxEM - minEM + stepEM) / stepEM)
numEX   <- ((maxEX - minEX + stepEX) / stepEX)
numAB   <- ((maxAB - minAB + stepAB) / stepAB)

# Load necessary libraries
library(MESS)

# Sets directories and lists files in the specified projdir
mstdir <- "C:\\Users\\E\\Documents\\School\\PHD\\DATA\\Fluorescence"  #  master data directory
prjdir <- paste(mstdir, project, "", sep="\\") #  set project directory
outdir <- paste(mstdir, "\\Corrected EEMs\\", project,"\\", sep="")
subdir <- list.dirs(path=prjdir)
subdir <- gsub(prjdir, "", subdir, fixed = TRUE)
subdir <- gsub("/", "", subdir, fixed = TRUE)
subdir[subdir!=""] <- paste(subdir[subdir!=""],"\\",sep="")

#loads the instrument correction curves
EXcor   <- read.csv(paste(mstdir, "\\Excorr.csv",sep=""), header=F, skip=2, nrows=381)
EMcor   <- read.csv(paste(mstdir, "\\Emcorr_220 to 600.csv",sep=""), header=F, skip=2, nrows=381)
colnames(EXcor) <- c("EXWAV","cor")
colnames(EMcor) <- c("EMWAV","cor")
EXcor[1] <- round(EXcor[1])
```

```
EXcor   <- EXcor[seq(which(minEX == EXcor$EXWAV), which(maxEX == EXcor$EXWAV), stepEX), 1:2]
EMcor   <- EMcor[seq(which(minEM == EMcor$EMWAV), which(maxEM == EMcor$EMWAV), stepEM),
1:2]


# Predefines output variables
allout <- data.frame(Folder = character(), rawEEMFile = character(), InstCorr=character(),
                     HIX = numeric(), FI = numeric(), BA = numeric(), SUVA = numeric (),
                     E2E3 = numeric(), SAC340 = numeric(), stringsAsFactors=FALSE)
out <- allout
skipped = FALSE

for (s in 1:length(subdir)) {  #  Loop through subfolders
  if (((presub==TRUE)|(s==1)) & (file.exists(paste(outdir, subdir[s], sep="")) == FALSE)) {
    dir.create(path = paste(outdir, subdir[s], sep=""), showWarnings=FALSE)
  }
  files  <- list.files(path = paste(prjdir,subdir[s],sep=""), pattern = ".csv", recursive=FALSE,
                       ignore.case=TRUE)
  files  <- subset(files, !grepl("blank|metrics|abs", files, ignore.case=TRUE))
  if (length(files) == 0) {
    skipped <- TRUE
    next
  }
  out[1:length(files), ] <- NA
  ABfile <- list.files(path = paste(prjdir,subdir[s],sep=""), pattern = "abs.*.csv",
                       ignore.case=TRUE)
  if (length(ABfile) > 1) {
    stop("More than one absorbance file found.")
  } else if (length(ABfile) == 0) {
    stop("No absorbance file found.")
  }
  allAB <- read.csv(file = paste(prjdir, subdir[s], ABfile, sep=""), nrows = numAB + 2,
                    header = FALSE, colClasses="character")

  for (f in 1:length(files)) {  #  Loop through files in each subfolder
    # Print file progress in Console
    cat("\r                                                                \r")
    if (s == 1 & f == 1) {
      cat(paste("Project:",project,"\n"))
    } else if (f == 1 & skipped == FALSE) {
      cat("\r                                                                \r")
      cat(paste("Folder ",s-1," of ",length(subdir)," (\\", subdir[s-1], "): Done!\n",sep=""))
    } else if (f == 1 & skipped == TRUE) {
      cat(paste("Folder ",s-1," of ",length(subdir)," (\\", subdir[s-1], "): No fluorescence files found.\n",sep=""))
      skipped = FALSE
    }
    cat(paste("Folder ", s, " of ", length(subdir), " (\\", subdir[s], "): ", files[f], " (File ", f, " of ",
              length(files) ,")", sep=""))
```

```
  # This section reads in the current raw EEM csv file in the current subfolder
  rawEEM <- read.csv(file = paste(prjdir, subdir[s], files[f], sep=""), header=FALSE,
                     skip=2, nrows=numEM)
  fileinfo <- read.csv(file = paste(prjdir, subdir[s], files[f], sep=""),
                               header=FALSE, nrows=1, as.is = 1)[1, 1]
  if (grepl("_cor",fileinfo, ignore.case=TRUE)) { #  if corrections done by Cary Eclipse
    inst_correct <- TRUE   #  then do not perform manually
    out$InstCorr[f] <- "Machine"
  } else {
    inst_correct <- FALSE  #  Perform manual instrument correction
    out$InstCorr[f] <- "Manual"
  }

  rawEEM <- rawEEM[, c(1,seq(from = 2, to = length(rawEEM), 2))]
  rawEEM[1] <- round(rawEEM[1])
  for (i in 1:(numEX + 1)) {
    if(i == 1) {
      colnames(rawEEM)[1] <- "EMWAV"
    } else {
      colnames(rawEEM)[i] <- paste("EX",minEX + (stepEX * (i-2)), sep="")
    }
  }
  match <- which(allAB[1, ] == gsub(".csv","",files[f],ignore.case=TRUE))
  if (length(match) == 0) {
    stop(paste("No matching absorbance sample found in: ", ABfile, sep=""))
  } else if (length(match) > 1) {
    stop(paste("More than one matching absorbance sample found in: ", ABfile, sep=""))
  }
  AB <- allAB[c(-1,-2), c(match,match+1)]
  colnames(AB) <- c("WL", "Int")
  AB$Int <- as.numeric(AB$Int)
  AB$WL <- round(as.numeric(AB$WL))
  AB <- AB[order(AB$WL), ]
  AB$Int[AB$Int < 0] <- 0

  # This does the Inner Filter Correction and Instrument Correction
  ex <- AB[seq(which(minEX == AB$WL), which(maxEX == AB$WL), stepEX), 1:2]  # match AB EX data
  em <- AB[seq(which(minEM == AB$WL), which(maxEM == AB$WL), stepEM), 1:2]  # match AB EM
data
  cEEM <- as.matrix(rawEEM)
  emif <- cEEM
  exif <- cEEM
  emic <- cEEM
  exic <- cEEM
  emif[1:151,2:(numEX+1)] <- replicate(numEX,em$Int)
  exif[1:151,2:(numEX+1)] <- t(replicate(numEM,ex$Int))
  emic[1:151,2:(numEX+1)] <- replicate(numEX,EMcor$cor)
  exic[1:151,2:(numEX+1)] <- t(replicate(numEM,EXcor$cor))
  minval <- min(cEEM[,2:48])
```

```
   if (minval < 0) { #  This shifts the EEM so that any negatives dissapear, lowest value becomes 0
     cEEM[,2:48] <- cEEM[,2:48] + abs(minval)
   }
   if (inst_correct == FALSE) {
     cEEM[,2:48] <- cEEM[,2:48] * exic[,2:48] * emic[,2:48]  # perform correction
   }
   cEEM[,2:48] <- cEEM[,2:48] * 10 ^ (0.5 * (exif[,2:48] + emif[,2:48])) #  Inner filter corr, 1 cm pathlength
   cEEM <- as.data.frame(cEEM)

   # This section calculates common metrics
   out$Folder[f] <- paste("\\",subdir[s],sep="")
   out$rawEEMFile[f] <- files[f]
   out$HIX[f]    <- (auc(cEEM$EMWAV, cEEM$EX255, from=434, to=480, type=c("linear"))) /
            (auc(cEEM$EMWAV, cEEM$EX255, from=300, to=346, type=c("linear")))
   out$FI[f]     <- cEEM$EX370[cEEM$EMWAV == 470]/cEEM$EX370[cEEM$EMWAV == 520]
   out$BA[f]     <- (cEEM$EX310[cEEM$EMWAV == 380]) /
            (max(cEEM$EX310[cEEM$EMWAV > 419 & cEEM$EMWAV < 437]))
   out$SUVA[f]   <- (AB$Int[AB$WL == 254]) / 0.01
   out$E2E3[f]   <- (AB$Int[AB$WL == 250]) / (AB$Int[AB$WL == 365])
   out$SAC340[f] <- 2303 * AB$Int[AB$WL== 340]

   # This section writes a corrected file prepared for PARAFAC
   if (presub==TRUE) {
     write.csv(cEEM,file = paste(outdir, subdir[s],files[f], sep=""), row.names = FALSE)
   } else {
     write.csv(cEEM,file = paste(outdir, files[f], sep=""), row.names = FALSE)
   }
  }  # End of loop through files
  allout <- rbind(allout,out)
}  #  End of loop through subdirectories
cat("\r                                                                    \r")
cat(paste("Folder ",s," of ",length(subdir)," (\\", subdir[s], "): Done!\nFinished.",sep=""))

# All files have now been looped through and corrected.
# This section writes the metrics into a single CSV file for all samples that have been run
metrics <- file(description = paste(outdir, project, "_Metrics.csv", sep=""), "w")
cat(paste("Project:", project, "\nScript ran on:", Sys.time(), Sys.timezone(), "\n\n", sep=" "),
   file = metrics)
write.table(allout, file=metrics, row.names=FALSE, sep=",", dec=".", qmethod="double")
cat("\nHIX: Humification Index\nFI: Fluorescence Index\nBA: Beta:alpha or freshness index\nSUVA: Specific
UV Absorbance @ 254nm (value must be divided by DOC in mg/L)\nE2E3: Absorbance ratio\nSAC340:
Specific absorption coefficient 2303*abs340 (must be divided by DOC in mg/L)",file = metrics)
close(metrics)
rm(list=ls()
```

A6. Parallel Factor Analysis (PARAFAC) Methods

PARAFAC modelling and validity

Fellman et al. (2009) found that fitting to existing PARAFAC models is difficult for samples that originate from soil water or that have high protein-like fluorescence. Fitting to existing models also requires careful methodological consideration to avoid inter-laboratory differences (Fellman et al., 2009; Murphy et al., 2010). Therefore, a unique model with 1216 samples from boreal lakes, streams, and wetlands representing a range of mining-, forestry-, urban-, and fire-related catchment disturbances was generated.

Prior to PARAFAC modelling, corrected EEMs were normalized by scaling to unit variance to remove covariance between fluorophores and down-weigh the influence of high concentration samples in loadings (Murphy et al., 2013). PARAFAC modelling was done in MATLAB using the N-Way and drEEM toolboxes (Andersson and Bro, 2000; Murphy et al., 2013), with non-negativity constrains but no a priori assumptions of number or shape of components.

Model validity was tested with visual analysis of residuals and spectral loadings, and with split-half analysis whereby models are generated on data subsets and compared to the complete model. Each split-half model was generated from random division of the original 1216 sample dataset in four groups (A,B,C and D) and pairing groups to form six independent split-half datasets of 608 samples each (AB, AC, AD, BC, BD, and CD). This provided three comparable test combinations: AB vs CD, AC vs BD, and AD vs BC (Figure A.3), for which a PARAFAC model should be the same if the correct number of components has been selected. Each test combination is compared by generating a Tuckers congruence coefficient for each component (Lorenzo-Seva and Berge, 2006), with > 0.95 required for each component for the comparison to

be considered validated. Validation was attempted starting with four components and adding additional components until validation failed. This validated a model with six unique fluorophores, explaining 99.6 % of the variation in the EEMs. Spectral loadings of all 6 splits compared to the full model (overall dataset) are plotted in Figure A.4.

The six PARAFAC components extracted in our model are all similar in shape and peak position to components in Stedmon and Markager (2005) and other recently conducted PARAFAC models. Our **C1** is considered fulvic-like, comparable to C4 identified in Stedmon and Markager (2005), and to fulvic components identified by Singh et al. (2013) and Hong et al. (2012). Our **C2** is also considered fulvic-like, similar to C2 identified by Stedmon and Merkager (2005), C2 in Ishii and Boyer (2012), and C3 in Hong et al. (2012). No functional difference has been identified between these first two fulvic-like components (our C1 and C2) in the literature. Our **C3** is considered humic-like, similar to the "M-shifted" lower-molecular weight C6 in Stedmon and Merkager (2005), and to C2 in Singh et al. (2005) and Hong et al. (2012). This component is considered to represent more labile and lower molecular-weight organic molecules compared to other humic-like components (Fellman et al., 2010), and an "M-shift" in humic material can represent a decrease in the number of aromatic rings or conjugated bonds (Coble, 1996). Our **C4** is also considered humic-like, but is similar to high-molecular weight humic C3 component identified by Stedmon and Markager (2005) and C1 in Ishii and Boyer (2012). Our **C5** and **C6** components are characteristic of tyrosine-like and tryptophan-like components respectively, similar to C8 and C7 components in Stedmon and Markager (2005) (Table A.9). These components are further reviewed by Fellman et al. (2010).

Quenching

Concentrations of several metals (e.g: Ni and Co) were elevated in stream water following the drought, while other metals (e.g: Cu) were closely associated with DOM and were higher during the onset of the drought (Chapter 3). Studies have suggested that quenching by metals such as Cu and Fe can affect peak fluorescence and influence spectral measures of DOM. Quenching tends to be most evident in laboratory settings rather than natural systems, likely because of the abundance of competing chelating agents (reviewed by Hudson et al., 2007), but there are some notable examples of quenching in natural systems (e.g.: Fe in Kelton et al., 2007). However, Reynolds and Ahmad (1995) found that quenching peaked at ~ 1 – 2 mg/L of Cu and Ni, and Piana and Zahir (2000) noted that the quenching effect of metals also tends to be greatest at high pH (~ 7 - 8), diminishing by as much as 20 times at pH of ~4. Indeed, recent studies have shown that the quenching effect in natural systems occurs in high-pH systems (Mounier et al., 2010; Yamashita and Jaffe, 2008). Given the low pH of our samples (~ 4 to 5) and the high concentrations of chelating metals both before and after drought (in some cases higher prior to drought, particularly the chelating metals Cu and Fe), it is unlikely that quenching is playing a major role in drought-related DOM changes.

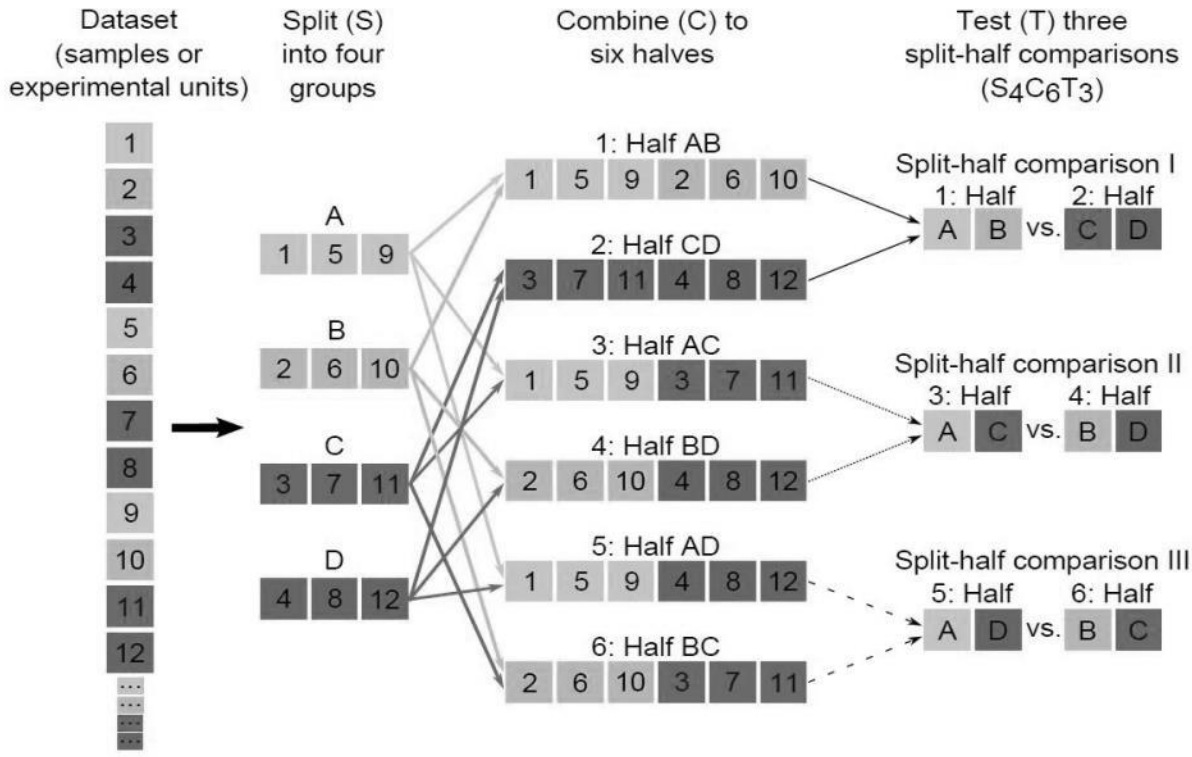

Figure A.3: Illustration of the sample division used to generate split-half datasets. Each split-half model was generated from random division of the original data in four groups (A, B, C, and D) and subsequently pairing groups (S) to form six independent datasets half the size of the original (AB, CD, AC, BD, AD, and BC). The new datasets (C) allow for three split-half comparisons (T), referred to by Murphy et al. (2010) as a $S_4C_6T_3$ combination. Figure is as shown in Appendix B in Murphy et al. (2010).

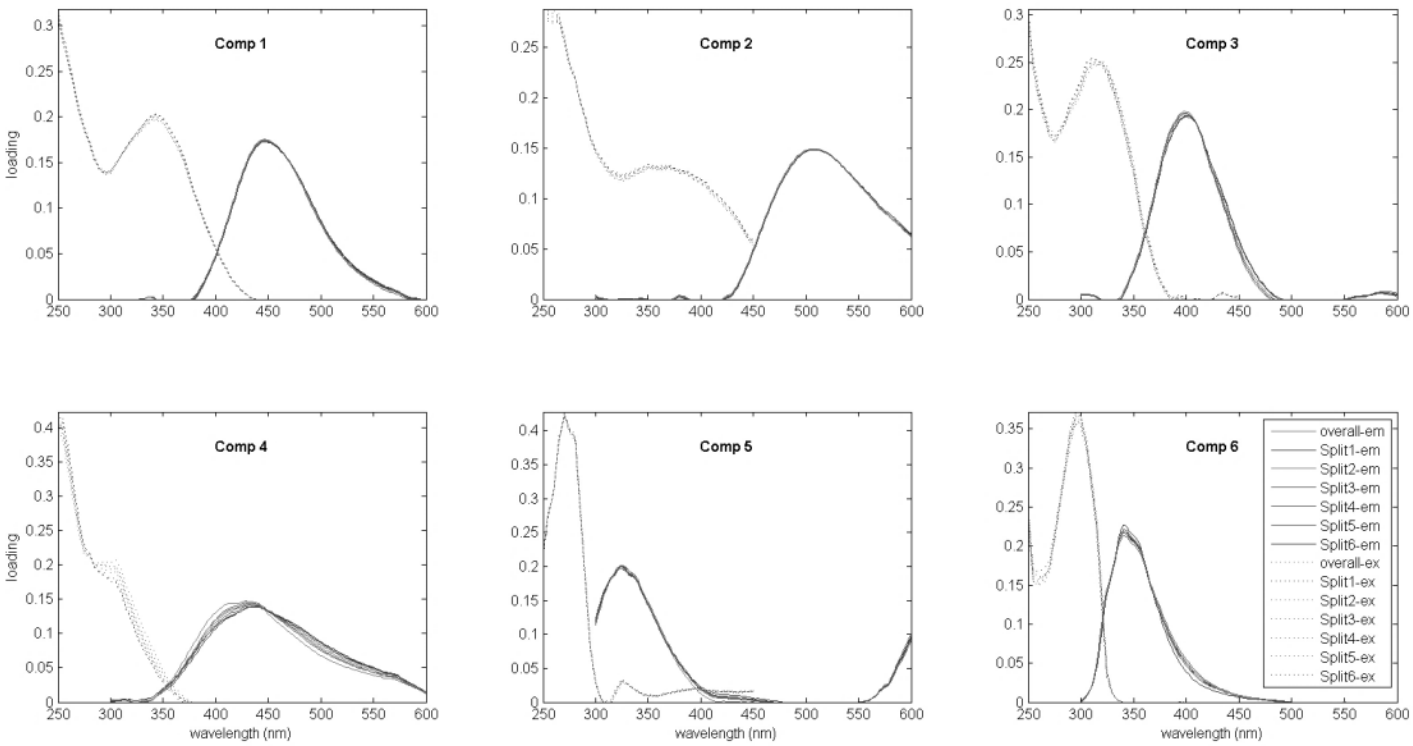

Figure A.4: Excitation (dotted) and emission (solid) loadings from six split-half models compared to loadings from the original derived from the whole dataset. Very little difference is observed, and each of the six split-half datasets was validated using Tuckers Correlation, providing strong evidence of original model validity.

Table A.9: Excitation and emission intensity peaks of the six modelled PARAFAC components, showing secondary excitation peaks in brackets. Humic components are identified as low molecular-weight (LMW) and high molecular-weight (HMW).

Component	Description	Excitation peaks	Emission peak
C1	fulvic-like	<250 (340)	446
C2	fulvic-like	255 (350)	504
C3	LMW humic-like	<250 (310)	400
C4	HMW humic-like	<250 (305)	434
C5	Tyrosine-like	270	324
C6	Tryptophan-like	295	340

A7. Biotic Ligand Modelling Data

Average Daisy Lake water chemistry was calculated from mid-lake samples collected by the Ontario Ministry of the Environment, with two collected in June and August (pre-drought) and two collected in September and October 2011 (post-drought). Lake Laurentian water chemistry was not available for 2011 so an average of monthly samples collected by the Nickel District Conservation Authority from May to September 2010 was used (Table A.10). The biotic ligand model was then run with average stream water and lake water mixed at stream:lake ratios of 1 to 0 at 0.1 ratio intervals, repeated for both pre- and post-drought conditions using DOC_{actv} (Scenario A: Table A.11 Table A.12). To assess the influence of DOM changes on toxicity, post-drought BLM accumulation calculations were repeated across all dilutions with DOM composition and concentration held at pre-drought conditions (Scenario C: Table A.12). The influence of DOM composition was assessed by calculating pre- and post-drought toxic units using DOC_{meas} for comparison with toxic units using DOC_{actv} (Scenario B: Table A.11, Table A.12). BLM models were also generated for the other four sites (C1, C2, BR, and D5) using three spring samples (from May and June 2011) and three fall samples (from October and November 2011) to represent pre- and post-drought periods respectively, for comparison to the high-frequency sampling sites (D4, LU) (Table A.13).

Table A.10: Daisy Lake and Lake Laurentian chemistry used to calculate pre-drought and post-drought averages for dilution of stream water in biotic ligand modelling.

Lake	Date	pH	Cu (µg/L)	Ni (ug/L)	DOC (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	DIC (mg/L)
Daisy	2011-06-21	6.71	8.9	55.3	2.5	2.36	1.19	1.19	0.335	8.4	0.95	1
	2011-08-17	6.73	6.8	42	2.5	2.16	1.21	1.31	0.335	7.2	1.01	1.1
	Pre-Drought Mean:	*6.72*	*7.85*	*48.7*	*2.5*	*2.26*	*1.2*	*1.25*	*0.335*	*7.8*	*0.98*	*1.05*
	2011-09-22	6.9	6.4	37.5	2.2	2.48	1.23	1.38	0.355	7.95	1.26	0.68
	2011-10-18	6.81	6.6	38.7	2.4	2.4	1.3	1.42	0.34	8	1.36	1.56
	Post-Drought Mean:	*6.86*	*6.5*	*38.1*	*2.3*	*2.44*	*1.27*	*1.4*	*0.3475*	*7.98*	*1.31*	*1.12*
Laurentian	2010-05-13	6.69	9.8	54.5	4.6	3.53	1.58	17.5	0.66	5.9	25.3	3.85
	2010-06-17	6.39	12.6	64.2	4.65	3.72	1.58	19.5	NA	5.6	29.9	10.3
	2010-07-19	6.52	14.4	51.7	6.35	4.4	1.62	22	0.35	5.3	32.1	4.75
	2010-08-19	6.97	15.7	48.8	5.78	4.12	1.84	21.8	0.26	NA	34.7	4.35
	2010-09-16	6.85	14.3	43.6	5.87	4.32	1.67	19.9	0.39	3.4	29.9	3.38
	2010 Mean:	*6.68*	*13.4*	*52.6*	*5.45*	*4.02*	*1.66*	*20.1*	*0.415*	*5.05*	*30.38*	*5.32*

Table A.11: Pre-drought chemistry and BLM-predicted accumulation of Cu and Ni on the biotic ligand (BLCu and BLNi) with stream water and lake water mixed at ratios of 0.0 (100 % stream water) to 1.0 (100 % lake water). Biotic ligand accumulations are presented for two scenarios: A. with measured DOC_{meas} in mg/L and B. with DOC_{actv} in mg/L. Stream and lake samples are averages of pre-drought conditions (see text).

	Mixing	pH	Cu (µg/L)	Ni (µg/L)	DOC_{meas} (mg/L)	DOC_{actv} (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	DIC (mg/L)	BLCu ($nmol/g_w$)		BLNi ($nmol/g_w$)	
														A	B	A	B
D4	0.00	4.77	31.1	61.3	3.21	2.57	0.759	0.308	0.874	0.431	5.11	0.753	0.466	4.15	5.30	0.812	0.909
	0.10	4.96	28.8	60.1	3.14	3.14	0.909	0.397	0.912	0.421	5.38	0.776	0.525	4.05	5.03	0.741	0.741
	0.20	5.16	26.5	58.8	3.07	3.07	1.06	0.487	0.949	0.412	5.65	0.798	0.583	3.70	4.50	0.688	0.688
	0.30	5.35	24.2	57.5	3.00	3.00	1.21	0.576	0.987	0.402	5.92	0.821	0.641	3.06	3.66	0.643	0.643
	0.40	5.55	21.8	56.3	2.92	2.92	1.36	0.665	1.02	0.393	6.19	0.844	0.700	2.23	2.64	0.605	0.605
	0.50	5.74	19.5	55.0	2.85	2.85	1.51	0.754	1.06	0.383	6.46	0.867	0.758	1.44	1.68	0.571	0.571
	0.60	5.94	17.2	53.7	2.78	2.78	1.66	0.843	1.10	0.373	6.72	0.889	0.817	0.841	0.959	0.539	0.539
	0.70	6.13	14.8	52.5	2.71	2.71	1.81	0.932	1.14	0.364	6.99	0.912	0.875	0.452	0.501	0.506	0.506
	0.80	6.33	12.5	51.2	2.64	2.64	1.96	1.02	1.17	0.354	7.26	0.935	0.933	0.229	0.246	0.470	0.470
	0.90	6.52	10.2	49.9	2.57	2.57	2.11	1.11	1.21	0.345	7.53	0.957	0.992	0.110	0.114	0.431	0.431
	1.00	6.72	7.85	48.7	2.50	2.50	2.26	1.20	1.25	0.335	7.80	0.980	1.05	0.050	0.050	0.389	0.389
LU	0.00	5.01	137	166	17.9	21.1	1.53	0.310	0.585	0.467	1.73	1.15	1.10	1.89	1.21	0.304	0.180
	0.10	5.17	125	155	16.7	16.7	1.78	0.445	2.54	0.462	2.06	4.08	1.52	2.44	1.85	0.429	0.429
	0.20	5.34	112	144	15.4	15.4	2.02	0.580	4.50	0.457	2.39	7.00	1.94	2.30	1.83	0.461	0.461
	0.30	5.51	100	132	14.2	14.2	2.27	0.714	6.45	0.452	2.73	9.92	2.36	1.86	1.51	0.464	0.464
	0.40	5.68	87.6	121	12.9	12.9	2.52	0.849	8.41	0.446	3.06	12.8	2.79	1.34	1.10	0.455	0.455
	0.50	5.84	75.2	109	11.7	11.7	2.77	0.984	10.4	0.441	3.39	15.8	3.21	0.882	0.731	0.438	0.438
	0.60	6.01	62.9	98.1	10.4	10.4	3.02	1.12	12.3	0.436	3.72	18.7	3.63	0.543	0.457	0.414	0.414
	0.70	6.18	50.5	86.7	9.19	9.19	3.27	1.25	14.3	0.431	4.05	21.6	4.05	0.316	0.272	0.380	0.380
	0.80	6.35	38.1	75.3	7.95	7.95	3.52	1.39	16.2	0.425	4.39	24.5	4.47	0.171	0.152	0.339	0.339
	0.90	6.52	25.7	63.9	6.70	6.70	3.77	1.52	18.2	0.420	4.72	27.5	4.90	0.083	0.077	0.291	0.291
	1.00	6.68	13.4	52.6	5.45	5.45	4.02	1.66	20.14	0.415	5.05	30.4	5.32	0.030	0.030	0.241	0.241

Table A.12: Post-drought chemistry and BLM-predicted accumulation of Cu and Ni on the biotic ligand (BLCu and BLNi) with stream water and lake water mixed at ratios of 0.0 (100 % stream water) to 1.0 (100 % lake water). Biotic ligand accumulations are presented for three scenarios: A. with measured DOC_{meas} in mg/L and B. with DOC_{actv} in mg/L, and C. with pre-drought DOC_{actv}. Stream and lake samples are averages of pre-drought conditions (see text).

	Mixing	pH	Cu (µg/L)	Ni (µg/L)	DOC_{meas} (mg/L)	DOC_{actv} (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	DIC (mg/L)	BLCu (nmol/g_w)			BLNi (nmol/g_w)		
														A	B	C	A	B	C
D4	0.00	4.08	36.7	217	3.06	2.17	2.87	1.13	1.39	0.716	17.2	2.50	0.624	5.66	6.70	6.20	2.59	2.69	2.64
	0.10	4.36	33.7	199	2.99	2.99	2.83	1.14	1.39	0.679	16.3	2.38	0.673	6.22	7.60	6.89	2.31	2.31	2.29
	0.20	4.63	30.6	181	2.91	2.91	2.78	1.16	1.39	0.642	15.3	2.26	0.723	6.50	8.00	7.18	2.04	2.04	2.02
	0.30	4.91	27.6	163	2.84	2.84	2.74	1.17	1.40	0.605	14.4	2.14	0.773	6.15	7.55	6.73	1.79	1.79	1.77
	0.40	5.19	24.6	145	2.76	2.76	2.70	1.18	1.40	0.568	13.5	2.03	0.822	4.95	6.06	5.35	1.55	1.55	1.53
	0.50	5.47	21.6	127	2.68	2.68	2.65	1.20	1.40	0.532	12.6	1.91	0.872	3.23	3.95	3.43	1.33	1.33	1.30
	0.60	5.74	18.6	110	2.61	2.61	2.61	1.21	1.40	0.495	11.7	1.79	0.921	1.69	2.04	1.75	1.11	1.11	1.08
	0.70	6.02	15.6	91.7	2.53	2.53	2.57	1.22	1.40	0.458	10.7	1.67	0.971	0.738	0.863	0.741	0.895	0.895	0.871
	0.80	6.30	12.5	73.8	2.45	2.45	2.53	1.24	1.40	0.421	9.82	1.55	1.02	0.285	0.318	0.275	0.686	0.686	0.665
	0.90	6.58	9.52	56.0	2.38	2.38	2.48	1.25	1.40	0.384	8.90	1.43	1.07	0.101	0.107	0.093	0.483	0.483	0.466
	1.00	6.86	6.5	38.1	2.30	2.30	2.44	1.27	1.40	0.348	7.98	1.31	1.12	0.032	0.032	0.028	0.294	0.294	0.281
LU	0.00	4.14	61.2	713	5.83	5.40	13.8	2.55	1.51	0.539	52.1	1.75	0.817	7.35	7.67	2.61	3.02	3.04	2.43
	0.10	4.39	56.4	647	5.79	5.79	12.8	2.46	3.37	0.526	47.4	4.61	1.27	7.95	8.30	2.79	2.84	2.84	2.31
	0.20	4.65	51.6	581	5.75	5.75	11.8	2.37	5.23	0.514	42.7	7.47	1.72	7.83	8.18	2.80	2.65	2.65	2.11
	0.30	4.90	46.9	515	5.71	5.71	10.9	2.28	7.10	0.501	38.0	10.3	2.17	6.72	7.02	2.42	2.43	2.43	1.91
	0.40	5.16	42.1	449	5.68	5.68	9.88	2.19	8.96	0.489	33.3	13.2	2.62	4.83	5.05	1.73	2.20	2.20	1.71
	0.50	5.41	37.3	383	5.64	5.64	8.90	2.10	10.8	0.477	28.6	16.1	3.07	2.84	2.97	1.04	1.94	1.94	1.51
	0.60	5.67	32.5	317	5.60	5.60	7.93	2.01	12.7	0.464	23.9	18.9	3.52	1.40	1.46	0.552	1.65	1.65	1.30
	0.70	5.92	27.7	251	5.56	5.56	6.95	1.93	14.6	0.452	19.2	21.8	3.97	0.603	0.622	0.272	1.32	1.32	1.07
	0.80	6.17	22.9	185	5.53	5.53	5.97	1.84	16.4	0.440	14.5	24.7	4.42	0.238	0.243	0.131	0.968	0.968	0.821
	0.90	6.43	18.1	119	5.49	5.49	4.99	1.75	18.3	0.427	9.75	27.5	4.87	0.088	0.089	0.063	0.600	0.600	0.542
	1.00	6.68	13.4	52.6	5.45	5.45	4.02	1.66	20.1	0.415	5.05	30.4	5.32	0.030	0.030	0.030	0.245	0.245	0.245

Table A.13: Spring (May and June 2011) and fall (October and November) water chemistry, averaged for BLM-predicted accumulation of Cu and Ni on the biotic ligand (BLCu and BLNi).

Site	Sample	pH	Cu (µg/L)	Ni (µg/L)	DOCactv (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO4 (mg/L)	Cl (mg/L)	DIC (mg/L)	BLCu (nmol/g_w)	BLNi (nmol/g_w)
BR	2011-05-12	4.78	12.4	59.0	2.67	0.970	0.550	0.580	0.390	12.6	1.08	0.970		
	2011-06-01	5.02	14.9	39.6	NA	0.848	0.298	0.720	0.409	0.260	0.070	0.280		
	2011-06-30	4.40	19.0	71.1	NA	1.298	0.448	0.932	0.279	7.42	2.62	0.410		
	Spring:	*4.73*	*15.4*	*56.6*	*2.67*	*1.04*	*0.432*	*0.744*	*0.359*	*6.75*	*1.26*	*0.553*	*2.65*	*0.810*
BR	2011-10-21	4.32	16.2	107	NA	3.24	0.955	1.09	0.832	13.4	1.53	0.488		
	2011-11-04	4.37	13.9	192	NA	3.27	1.08	1.17	1.082	14.0	2.01	0.821		
	2011-11-18	4.33	18.2	148	3.98	2.57	0.877	1.48	0.333	10.5	0.917	0.900		
	Fall:	*4.34*	*16.1*	*149*	*3.98*	*3.03*	*0.971*	*1.24*	*0.749*	*12.6*	*1.49*	*0.736*	*2.38*	*1.64*
C1	2011-05-12	5.06	34.2	84.7	8.14	1.83	0.580	1.33	1.23	4.79	1.38	0.840		
	2011-06-01	5.44	47.6	3.45	10.7	1.431	0.558	1.58	0.564	1.19	1.99	0.770		
	2011-06-30	5.34	40.5	90.8	16.1	1.419	0.494	1.43	0.418	1.20	0.900	1.20		
	Spring:	*5.28*	*40.8*	*59.7*	*11.6*	*1.56*	*0.544*	*1.45*	*0.738*	*2.39*	*1.42*	*0.937*	*1.11*	*0.217*
C1	2011-10-05	5.28	10.2	154	3.11	7.16	2.39	3.12	0.714	33.3	2.30	2.95		
	2011-10-21	3.59	24.8	222	NA	5.86	2.13	1.67	1.53	25.1	1.16	1.29		
	2011-11-04	3.90	17.1	256	4.79	4.86	1.75	1.48	0.429	22.0	1.12	0.970		
	Fall:	*4.26*	*17.4*	*210*	*3.95*	*5.96*	*2.09*	*2.09*	*0.891*	*26.8*	*1.53*	*1.74*	*2.93*	*1.64*

Table A.13: Continued.

Site	Sample	pH	Cu (µg/L)	Ni (µg/L)	DOCactv (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO4 (mg/L)	Cl (mg/L)	DIC (mg/L)	BLCu (nmol/g_w)	BLNi (nmol/g_w)
C2	2011-05-12	5.36	22.2	57.7	6.89	8.4	1.27	8.22	1.25	8.28	31.3	1.11		
	2011-06-01	5.21	21.2	110	4.24	18.4	2.67	17.2	1.07	5.32	64.1	1.05		
	2011-06-30	4.86	13.5	40.6	10.3	4.509	0.611	5.75	0.436	3.57	39.7	0.97		
	Spring:	*5.14*	*19.0*	*69.6*	*7.15*	*10.4*	*1.52*	*10.4*	*0.919*	*5.72*	*45.0*	*1.04*	*1.73*	*0.319*
C2	2011-10-21	4.82	24.7	36.6	10.4	14.2	1.77	7.90	1.77	18.4	32.1	0.762		
	2011-11-04	4.82	19.5	131	7.78	15.0	2.29	9.48	1.187	17.6	32.8	0.756		
	2011-11-18	4.88	23.6	101	7.53	12.0	1.87	9.30	0.847	14.8	30.2	0.858		
	Fall:	*4.84*	*22.6*	*89.5*	*8.55*	*13.7*	*1.98*	*8.89*	*1.27*	*16.9*	*31.7*	*0.792*	*2.52*	*0.348*
D5	2011-05-12	5.69	12.0	94.2	NA	2.76	0.842	1.55	0.484	7.83	3.04	0.880		
	2011-06-01	5.23	24.8	81.4	2.13	0.647	0.291	0.995	0.169	9.62	0.740	0.950		
	2011-06-30	5.80	4.33	18.5	3.92	0.622	0.256	0.740	0.385	6.69	1.35	2.59		
	Spring:	*5.57*	*13.7*	*64.7*	*3.03*	*1.34*	*0.463*	*1.10*	*0.346*	*8.05*	*1.71*	*1.47*	*1.19*	*0.976*
D5	2011-10-06	5.33	7.34	111	1.99	4.60	2.14	2.08	0.939	20.9	2.48	2.47		
	2011-10-19	5.11	7.50	225	1.91	5.98	2.92	2.37	1.09	21.7	3.31	0.671		
	2011-11-02	4.34	7.14	163	2.16	3.87	1.48	1.35	0.440	15.3	3.05	0.558		
	Fall:	*4.93*	*7.33*	*166*	*2.02*	*4.82*	*2.18*	*1.93*	*0.825*	*19.3*	*2.95*	*1.23*	*2.68*	*1.49*

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